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LITERATURE REVIEW OF METROPOLITAN AIR POLLUTANT CONCENTRATIONS-PREPARATION, SAMPLING AND ASSAY OF SYNTHETIC ATMOSPHERES

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Stanford Research Institute
Menlo Park, California

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Final Report

LITERATURE REVIEW OF METROPOLITAN AIR POLLUTANT CONCENTRATIONS-- PREPARATION, SAMPLING AND ASSAY OF SYNTHETIC ATMOSPHERES

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STANFORD RESEARCH INSTITUTE
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FINAL REPORT

LITERATURE REVIEW OF METROPOLITAN AIR POLLUTANT CONCENTRATIONS -- PREPARATION, SAMPLING, AND ASSAY OF SYNTHETIC ATMOSPHERES

I Introduction

Pollution in the atmosphere over metropolitan areas may have a considerable effect on the viability of airborne micro-organisms. The concentration, chemical identity, and number of pollutants varies with the fuel and industrial economy as well as with the population of metropolitan areas.

It is important in assessing the action of airborne micro-organisms to know which of the many air pollution components may interact with these organisms. Also, the critical pollution concentrations above which such organisms may not remain viable must be known and be relatable to population level and economy.

Because of the nature of micro-organisms, they cannot be tested in the polluted atmospheres of cities. Typical concentrations of pollution simulants which can be created in controlled test atmospheres are necessary, therefore, to accomplish the desired evaluation.

Stanford Research Institute was asked to conduct a literature review and to make extensive tabulations of measured concentration of all pollutants found in metropolitan atmospheres in connection with air pollution investigations. These results, which comprised the first phase of the study, were to be related to broad class intervals of population increments and to the fuel and industrial economies.

The second phase of the study involved selection of a complete pollution simulant formulation representative of the average maximum concentrations of all known atmospheric pollution components. Methodology, techniques, and equipment for preparation, sampling, and assay of the proposed test formulation were to be created for use in connection with a static test chamber held at a slight negative pressure.

II Summary

Sufficient work has been accomplished in the course of many air pollution studies to reveal a rather extensive list of measured chemical components. These are revealed in the results of this project and are presented in detail in Appendix A.

In the course of the years during which these studies have been carried out, a continuous state of flux has prevailed not only in the concept of what air pollution is and does, but also in the thoroughness and accuracy with which sampling and analytical procedures have been carried out. Certainly little thought has been expended in designing these many studies to produce results which would be uniformly revealing or universally comparable. Most studies were planned to deal with specific nuisances in a particular metropolitan community. In the light of recent findings, however, air pollution has been found to exist as a complex chemical system in which known or suspected interactions play an important role in determining its integrated effect.

Published air pollution data that are adequately related to the fuel and industrial economies are too few to be statistically representative. A unique approach was tried in the course of this project for calculating pollutant component concentrations, using as basic data published economic statistics on domestic and industrial fuel consumption. These data have been resolved with respect to seven metropolitan centers. Assumptions were made to establish bases for computation of combustion product emissions. From knowledge of the industrial processes involved in the basic industrial classifications, process emissions were calculated in accordance with fuel consumption data. Once total emissions of pollution components usually present in significant concentration in the atmosphere were obtained the average concentration could be calculated. The volume of air used as a basis for these calculations was obtained by using the published area of each metropolitan center and assuming meteorologically significant inversion heights and average daily wind movements. The results of these computations are presented in Appendix B, and are believed in the light of our experience to be representative results. Concentration versus population curves for a number of pollutants are also presented in the belief that such data may be helpful in establishing the quantity of micro-organisms which produce definite effects.

Summary tabulations of measured and calculated pollutant concentrations were prepared; they are presented in Appendix C. These tabulations are intended to assist in the design of additional test formulations in the event that the prime formulation proposed in Appendix D yields results which prove excessively effective in diminishing the viability of airborne micro-organisms to be tested.

The selection of a composite formulation of air pollution components for use in preparation of a simulant atmosphere in static chamber tests was based on measured, average maximum concentrations revealed by the literature review, the calculated air concentrations, and knowledge of air pollution problems.

The methods, techniques, and equipment for the preparation of a static synthetic atmosphere were designed to minimize manipulatory detail immediately associated with the injection of simulant components into the chamber. The procedure and equipment specified, when applied in connection with the proposed complex test-formulation, have not been fully tested. However, it is our belief that the proposed methodology is consistent with good practice and that a minimum trial period will be involved in perfection of a procedure leading to desired concentrations in the test chamber.* Appendix D contains full details on procedures as well as commercial sources of material and most of the equipment. Some equipment is specified which must be specially fabricated, but the number of these items is held to a minimum.

The sampling and quantitative analysis procedures proposed in Appendix E were selected with several requirements in mind, the most important of which is simplicity consistent with reasonable accuracy.

Complex and costly analytical equipment such as the emission spectrometer, infrared spectrometer, mass spectrometer, and combination sampling and analytical equipment such as the autometer, Titrilog, and oxidant and fluoride recorders were omitted.

The Greenburg-Smith impinger preceded by a millipore filter is specified as the major sampling equipment in the belief that this equipment is the simplest and most effective for this purpose. The principal advantage lies in minimization of the number of samplers necessary in sampling complex synthetic atmospheres.

Where possible, two analytical methods are described; a rapid method and a complex but more accurate method. In so doing, it was reasoned that both methods could be run during prefatory phases of the test program. This would allow a calibration of the rapid method against the more accurate so that as the complexity of the synthetic atmosphere was increased, analytical procedures necessary for monitoring the test atmosphere would become progressively less complex.

Decomposition products of explosives and propellants as well as sampling and analytical procedures for decontamination agents were covered extensively in Progress Report Nos. 2 and 4, respectively, and are not repeated in the final report.

Recommendations for provision of appropriate illumination within the test chamber to simulate the effect of short wavelength components of solar radiation are made. The matter of air circulation within the test chamber and its effect on the persistence of the particulate components is also discussed. Chamber lining characteristics are discussed as well.

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* Sampling and wall losses (assuming proper chamber lining) should not exceed fifteen percent.

The exact chemical nature of many components stipulated in the proposed test formulations of Appendix D represents arbitrary choices. Every effort was made to choose for each item of the formulation a chemical compound which is related either to an industrial and fuel economy or to naturally occurring forms. This applies more to the particulate and some of the organic components.

The amount of each component specified in the proposed formulation is intended to be the theoretical quantity representing typical average maximum concentration as revealed by the literature review. The actual quantities of these components which must be injected into a test chamber will depend on adsorption and impaction losses as well as on chemical interactions which may be involved. Also, the size of the initial sample for control purposes must be taken into consideration in establishing actual amounts to be injected.

Prediction of probable chemical interactions among components or reaction rates is not possible in advance of the tests. The extent to which these interactions occur will be revealed during the course of testing with subgroups.

In the analytical procedures, interferences among components of the test formulation are indicated individually. Many of these procedures have been used in assaying the atmosphere. Therefore, the results from application of these procedures to a synthetic atmosphere should be comparable to similar results of studies made on the open atmosphere.

Because of the complexity of the total formulation proposed, preliminary postulations made regarding the methodology of preparing the synthetic atmosphere must be subject to experimental verification.

The proposed test formulation, which reflects the average maximum concentrations of all known pollution components, is presented to serve as a point of departure in the testing of airborne micro-organisms. Revisions in the formulation which may be indicated by initial tests can be drawn from various tabulations in Appendixes A, B, and C.

Simulation of the effects of solar radiation may be accomplished with the use of 40-watt, fluorescent-type sun lamps* mounted in the test chamber. Eight lamps may be arranged vertically at cardinal points on the chamber wall. Such an array should be sufficient to approximate the effects of solar radiation within a time interval of the order of minutes. This limitation in time of exposure would be necessary in order not to allow excessive degradation of the synthetic atmosphere before injection of the micro-organisms.

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* Westinghouse Electric Corp., Bloomfield, N.J., Type FS40T12, available in standard packages of 1/2-dozen. The relative energy distribution of this type peaks at about 3100 Angstrom units with a spectral range of 2900 to 3400 above 30%. The average life of this type when operated 15 minutes per start is about 1200 hours. The tube surface must be kept clean in order to achieve reproducible results. The Westinghouse SM-200 meter may be used to evaluate the degradation of light output resulting from tube aging.

Provision should be made in the amount of pollutant simulants originally injected to allow for withdrawal of the extra samples necessary to monitor possible photochemical reactions.

In order that impaction losses can be kept to a minimum, care must be exercised on speed control of the circulating fan within the chamber. Tests should be run with a particulate charge in the test chamber to determine the best fan speed and orientation of the fan-driven air current. The fan speed should be such that the axial velocity of the air stream decays to near zero before reaching the chamber wall. Best orientation of the fan-driven air current is more apt to be diametric from base to top of cylindrical chamber than with axial sweep from center of chamber base.

Chamber lining is important in determining concentration decay. In the course of discussions with Dr. E. B. Seligmann, an infrared, baked coating of Uformite-12* pigmented with about 15 percent of carbon black was suggested as a suitable coating to minimize absorptive and adsorptive effects. Recommendations of the manufacturer for application to metal surfaces should be followed as nearly as possible.

No attempt is made to stipulate temperature and humidity control since these variables are understood to be dictated by requirements of the tests. Care should be exercised, however, in preventing condensation of water vapor on the test chamber wall when high moisture loadings are a part of the prime test procedure.

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* Resinous Products Corp., Division of Rohm & Haas, 712 Locust St., Philadelphia, Pa.

Appendix A

MEASURED CONCENTRATIONS OF GASEOUS AND PARTICULATE POLLUTANTS IN THE ATMOSPHERE

The necessity for an orderly and fully encompassing compilation on the range of and average concentration of all known atmospheric pollutants resulted in extensive perusal of air pollution literature and of the document files of Stanford Research Institute. These files contain both published and unpublished information and include data on measured concentrations of pollutants made as early as 1926 and as late as April 1956.

The amount of information available, unfortunately, is not the same for all presently known air pollutants. This is due to the variant emphasis which has been placed on the importance of different pollutants in the course of air pollution study and experience. The concept of representative results has changed in some instances as more rigorous and sensitive analytical techniques have been developed. The presence and importance of some pollutants have only recently been recognized. There are, for example, considerable quantities of data on sulfur dioxide concentration in the atmosphere and only a very few data for a small number of urban areas on the concentration of hydrocarbons in the atmosphere.

The tabulations which follow undoubtedly do not contain as much data as would result from longer effort to uncover unpublished information. Expediency has demanded otherwise. However, the data contained herein is believed to be representative of the findings to date. Any additional data very likely would serve only to reveal more unusual singularities, and with the possible exception of fluorides, the average concentrations tabulated herein would not be changed materially.

The tabulations of gaseous pollutant concentrations (Tables A-I through A-XI) are arranged according to chemical identification relative to the cities and dates of measurement. The concentrations are defined as average, minimum, and maximum. In the third category the values tabulated are average maxima unless stipulated in the "remarks" column as absolute maxima or "highest reported values." Where available, the number of samples used in compiling the figures is given, as are the classes of urban areas represented by the data. All concentrations are expressed in ppm by volume.

The tabulations of particulate concentration are arranged in three groups. The first group are gross particulate loadings of the air (Table A-XII) expressed as micrograms per cubic meter (μg/cu m), and are arranged by city and date of measurement. Average, average minimum, and average maximum loadings are given when available, as are the duration and methods of sampling and the classes of urban areas. Some data for rural areas are also given. The second group (Table A-XIII) are arranged according to specific metals expressed as µg/cu m. When available, duration of sampling, unusual chemical constituents, and classes of urban areas are shown. The data are from many studies, each of which was analyzed for a limited group of metals. In some cases, where duplicate data appear for a number of cities, only average concentrations for a group of cities of similar pollution level at the time of measurement were available. Table A-XIV shows the dustfall measurements of various cities.

Many different sampling and analytical techniques are represented by these data. Time did not permit nor was sufficient information available to allow a detailed assessment of the methods used in order to reveal inherent errors in the various results. In the course of the last ten years, improvements have been made in many of the techniques, which increase the representativeness of the sample and/or guarantee better analytical results, especially where interference by other constituents and chemical change in the sample are likely to prevail. The duration of sampling is, necessarily, a widely variant aspect of the conditions under which samples are procured. This is dictated by the relative amounts of pollutants likely to be present in the atmosphere and the sensitivity of the analytical method. The data in this compilation, therefore, do not represent similar sampling volumes. Where there is considerable variability in the concentration of atmospheric pollutants, long-period samples may give results which on the average are lower than results from samples collected in a short interval of time. Data from continuous methods of monitoring the atmosphere may reveal higher absolute maxima than do "batch" methods such as impingers and scrubbers which involve finite quantities of chemical reactants and longer sampling times.

The location of sampling stations was not always specified in the data sources. For this reason it is not possible to assess the representativeness of the data for a particular city for which only limited amounts of data are available. Where such information is not available it has been presumed that the sampling has occurred in an area which is suspect and that the data given are representative of the average industrial or commercial areas in that city.

Some of the ways in which analytical and sampling methods affect results are as follows. It is not always possible with some analytical methods used to distinguish the most chemically reactive form (at concentrations found in the atmosphere) of a given pollutant or type of pollutant. Pollutants which fall into this class are oxides of nitrogen, ammonia, aldehydes, total oxidants, and organics. The separation of gaseous and solid forms of a chemical pollutant has not always been accomplished fully in the collection of samples except where the latter are completely insoluble in the collecting or reacting media. Pollutants which are easily oxidizable may with certain analytical or sampling methods yield results which obscure the less stable form.

Certain analytical methods are sensitive to the interference of kindred chemicals which alter the representativeness of the resulting data. For example, particulate fluorides analysis gives erroneous results if aluminum ions and/or silica are present and the thorium-alizarin or similar method of analysis is used without pretreatment of the sample. Where many related components are present in a single sample, several aliquots are needed for separate treatment. This reduces the sample size for each analysis to the point where the lower limit of sensitivity of some analytical methods is exceeded. All these aspects and more contribute to the heterogeneity of the data.

We sought to select data for these compilations with consideration of their source and with our understanding of the care that was involved in their procurement. This limited the size of the tabulations. They are, however, considered to be representative listings of the required data and are the basis of this report.

Table A-I

ATMOSPHERIC SULFUR DIOXIDE CONCENTRATIONS (ppm by vol)

City	Date	Avg.	Min.	Max.	Ref.	Remarks and Number of Samples(a)
Akron, Ohio	1955	0.05	<0.01	0.12	1	Iodine method
		0.09	<0.01	0.22		Tot.SO_4,alkali trap
Altoona, Pa.	Sep/36	0.008	--	0.024	2	
Ann Arbor, Mich.	1955	<0.02	<0.01	<0.02	1	Iodine method
Atlanta, Ga.	1936-37	0.012	--	0.032	3	15-mi radius of city center
	Feb/37	0.032	--	0.094	2	
	May/37	0.012	--	0.069		
Baltimore, Md.	1936-37	0.021	--	0.081	3	15-mi radius of city center
	Sep/36	0.019	--	0.081	2	
	Feb/37	0.081	--	0.210		
	May/37	0.022	--	0.366		
	1950	0.074	0.01	0.47	4	Industrial (79)
		0.023	0.00	0.11		Rural (17)
Bellaire, O.	Aug/37	0.070	--	0.320	2	
Berlin, Germany	1926	--	0.5	0.7	5	
Bessemer, Ala.	Jan/37	0.017	--	0.114	2	
	Jun/37	0.017	--	0.087		
Birmingham, Ala.	Jan/37	0.017	--	0.114	2	
	Jun/37	0.017	--	0.087		
Buffalo, N.Y.	Dec/36	0.044	--	0.168	2	
Camden, N.J.	1936-37	0.030	--	0.424	6	0-5 mi from city center
		0.018	--	0.228		5-10 " " "
		0.016	--	0.335		10-15 " " "
		0.021	--	0.415		15-20 " " "
		0.012	--	0.062		20-25 " " "
		0.012	--	0.073		25-30 " " "
Charleston, W. Va.	Jan-Jun/51	0.079			7	Central area
		0.124				South area
		0.056				North area
	1950-51	0.023	0.001	0.180	4	(143)
	1955	0.04	<0.01	0.26	<1	Iodine method
		0.11	<0.01	0.63		Tot.SO_4,alkali trap
Charlotte, N. C.	May/37	0.015	--	0.05	2	
Chattanooga, Tenn.	1936-37	0.011	--	0.035	3	15-mi radius of city center
	Jan/37	0.035	--	0.102	1	
	Jun/37	0.011	--	0.044		

(a) Number of samples in parentheses

Table A-I (Cont'd.)

City	Date	Avg.	Min.	Max.	Ref.	Remarks and Number of Samples
Chicago,Ill.	1936-37	0.067	--	0.091	3	15 mi radius of city center
	Dec/36	0.109	--	0.402	1	
	Apr/37	0.073	--	0.549		
	Aug/37	0.067	--	1.141		
		0.67	Tr	2.54	4	Railroad station(32)
		0.50	0.17	3.16		Manufacturing area(99)
		0.41	Tr	3.16		Commercial area(89)
		0.16	Tr	0.47		Residental area(32)
Cincinnati, O.	Jan/37	0.064	--	0.270	2	
	Mar/37	0.064	--	0.295		
	Jun/37	0.021	--	0.107		
	1947-51	0.064	0.00	0.46	4	Ind. & Comm. (227)
		0.044	0.00	0.27		Residential (71)
		0.037	0.00	0.31		Rural (69)
		0.061	0.00	0.46		All areas (298)
	1955	0.04	<0.01	0.22	1	Iodine method
		0.07	<0.01	0.33		Tot.SO_4, alkali trap
Cleveland, O.	Oct/36	0.029	--	0.451	2	
	Dec/36	0.133	--	0.586		
	Apr-May/37	0.064	--	0.281		
	1949-50	0.042	0.00	0.489	4	Industrial (290)
Columbia,S.C.	Feb/37	0.018	--	0.090	2	
Detroit, Mich.	1936-37	0.028	--	0.396	3	15-mi radius of city center
	1936-37	0.023	--	0.228	6	Conc.-variable distance 0-5 mi from city center
		0.012	--	0.140		5-10 " " "
		0.006	--	0.139		10-15 " " "
		0.004	--	0.056		15-20 " " "
		0.004	--	0.044		20-25 " " "
		0.005	--	0.144		25-30 " " "
	1951-52				8	

Range	% Tot. Obsvd.	Total Avg. (No.)
0.00 - 0.05	67.5	(2524)
0.06 - 0.10	26.9	(1006)
0.11 - 0.15	4.7	(176)
0.16 - 0.20	0.87	(32)
0.21	0.05	(2)

City	Date	Avg.	Min.	Max.	Ref.	Remarks and Number of Samples
	1955	0.03	<0.01	0.13	1	Iodine method
		0.02	<0.01	0.10		Tot.SO_4, alkali trap
Donora,Pa.	1949	0.150			9	
	1949	0.150	0.00	>0.50	4	(529)
Elizabeth, N.J.	1955	0.12	<0.01	0.38	1	Iodine method
		0.20	<0.01	0.38		Tot.SO_4, alkali trap

Table A-I (Cont'd.)

City	Date	Avg.	Min.	Max.	Ref.	Remarks and Number of Samples
Fort Wayne, Ind.	1936-37	0.028	--		3	15-mi radius of city center
	Apr/37	0.028	--	0.309	2	
Gary, Ind.	Dec/36	0.109	--	0.402	2	
	Apr/37	0.073	--	0.549		
	Aug/37	0.067	--	1.141		
Hammond, Ind.	Dec/36	0.109	--	0.402	2	
	Apr/37	0.073	--	0.549		
	Aug/37	0.067	--	1.141		
Harrisburg, Pa.	1936-37	0.011			3	15-mi radius of city center
				0.309	2	
				0.037	6	
Indianapolis, Ind.	1936-37	0.023			3	15-mi radius of city center
				0.093	2	
Johnstown, Pa.	Sep/36	0.014		0.038	2	
London, England	Nov/48	0.46	--	0.67	10	Severe fog-avg.central sites
		0.19	--	0.31		" " " outer
	Dec/52	0.35	--	0.56		" " " "
		0.91	--	1.26		" " " central
	Dec/51	--	0.04	0.23		Avgs.-Greater London
	Dec/52	--	0.01	1.34		Most severe fog to date
Los Angeles, Calif.	1936-37	0.01	--	0.6	3	15-mi radius of city center
	1949-50	0.05	--	--	9	Good visibility
		0.20	--	--		Reduced visibility
			Tr	0.60	4	
	1950-52	0.1		0.60	11	Smoggy day
	1953?	0.05			12	Clear day-downtown
		0.3				Smog,intense-downtown
	Sep-Nov/54	--	0.05	0.10	13, 14	Downtown
	5/18/55			1.7	15	Max.conc.to date (El Segundo)
Louisville, Ky.	Jan/37	0.049	--	0.201	2	
	Mar/37	0.032	--	0.142		
	Jun/37	0.022	--	0.[illegible]19		
Martins Ferry, O.	Sep/37	0.070	--	0.320	2	
McGregor, Ontario	1951-52				9	
	Jan	0.0065	0.0015	0.010		
	Feb	0.0025	0.0019	0.0030		
	Mar	0.0037	0.0032	0.0043		
	Apr	0.0033	0.0008	0.0057		
	May	0.0039	0.0033	0.0045		
	Jun	0.0051	0.0039	0.0063		

Table A-I (Cont'd.)

City	Date	Avg.	Min.	Max.	Ref.	Remarks and Number of Samples
McGregor, Ontario (cont'd.)	Jul	0.0031	0.0012	0.0050		
	Aug	0.0045	0.0039	0.0050		
	1950-52					
	Sep	0.0095	0.0035	0.0150		
	Oct	0.0075	0.0035	0.0120		
	Nov	0.0073	0.0050	0.0110		
	Dec	0.0167	0.0100	0.0270		
Nashville, Tenn.	1936-37	0.028	--	0.093	3	15-mi radius of city center
	Jan/37	0.093	--	0.212	2	
	Jun/37	0.028	--	0.119		
Philadelphia Pa.	1936-37	0.027	--	0.424	3	15-mi radius of city center
	1936-37				6	Conc-variable distance
		0.030	--	0.424		0-5 mi of city center
		0.018	--	0.228		5-10 " " "
		0.016	--	0.335		10-15 " " "
		0.021	--	0.415		15-20 " " "
		0.012	--	0.062		20-25 " " "
		0.012	--	0.073		25-30 " " "
		0.022	--			Total average
	1955	0.08	0.01	0.17	1	Iodine method
		0.09	<0.01	0.22		Tot.SO_4, alkali trap
Pittsburgh, Pa.	1927				16	
	Aug	0.11				Avg.wind vel.-6 mph
	Sep	0.35				" " " 7 mph
	Oct	0.67				" " " 7 mph
						10/15/27: (dense smog) SO_2 conc.at 9AM-1.1 ppm; (bright,clear) SO_2 conc.at 12N-0.2 ppm
	Nov	0.10				Avg.wind vel.-13 mph
	Dec	0.09				" " " 14 mph
	1928					
	Jan	0.09				" " " 13 mph
	Feb	0.15				" " " 11 mph
	Mar	0.16				" " " 11 mph
	Apr	0.04				" " " 13 mph
	May	0.10				" " " 7 mph
	Jun	0.03				" " " 10 mph
	Jul	0.02				" " " 6 mph
	Aug	0.06				" " " 6 mph
	1931-32	0.30	0.00	2.5	4	Industrial (607)
	1936-37				6	conc.-variable distance

Table A-I (Cont'd.)

City	Date	Avg.	Min.	Max.	Ref.	Remarks and Number of Samples
Pittsburgh, Pa.(cont'd.)		0.060	--	0.828		0-5 mi of city center
		0.030	--	0.449		5-10 " "
		0.015	--	0.157		10-15 " "
		0.018	--	0.218		15-20 " "
		0.009	--	0.113		20-25 " "
		0.010	--	0.084		25-30 " "
		0.038	--			Total average
		0.057	--	0.897	3	15-mi radius of city center
Richmond,Va.	1936-37	0.009	--	0.047	3	" " " "
	Feb/37	0.047	--	0.261	2	
	May/37	0.009	--	0.025		
St.Louis,Mo.	1936-37	0.128	--	2.266	3	East St. Louis
	1936-37				6	conc.-variable distance
		0.111	--	1.080		0-5 mi of city center
		0.048	--	0.529		5-10 " "
		0.029	--	0.266		10-15 " "
		0.020	--	0.205		15-20 " "
		0.018	--	0.209		20-25 " "
		0.014	--	0.153		25-30 " "
		0.060				Total average
	1937	0.127			9	Warm months
		0.250				Cold months
	1950	0.042				Cold months
	1937	0.250	0.00	1.86	4	Cold months (663)
		0.127	0.00	0.756		Warm months (673)
	1950	0.041	0.00	0.51		Cold months (243)
		0.03	0.00	0.24		Warm months (294)
	1955	0.06	0.01	0.17	1	Iodine method
		0.10	<0.01	0.43		Tot.SO_4,alkali trap (27)
Salt Lake City, Utah	1919-20	0.036			4	
	1926	--	0.00	0.8	5	
Santa Clara, Calif.	1949-54	--	--	0.06	17	Highest reported value (spotty sampling)
Springfield, Mo.	1936-37	0.021			3	15-mi radius of city center
	Sep/37			0.169	2	
Toledo,O.	1936-37	0.023			3	" " " "
	Apr/37			0.072	2	
Washington, D.C.	1936-37	0.009	--	0.290	3	" " " "
	1936-37				6	Conc.-variable distance
		0.003	--	0.086		0-5 mi of city center
		0.001	--	0.047		5-10 " " "
		0.001	--	0.035		10-15 " " "
		0.001	--	0.036		15-20 " " "
		0.001	--	0.012		20-25 " " "
		0.002	--	0.047		25-30 " " "
		0.002	--			Total average

Table A-I (Cont'd.)

City	Date	Avg.	Min.	Max.	Ref.	Remarks and Number of Samples
Washington, D.C.(cont'd.)	1955	0.04	<0.01	0.12	1	Iodine method
		0.09	<0.01	0.35		Tot.SO$_4$, alkali trap
Wheeling, W. Va.	1936-37	0.070			3	15-mi radius of city center
	Aug/37	--	--	0.320	2	
Whiting, Ind. (Chicago)	Dec/36	0.109	--	0.402	2	
	Apr/37	0.073	--	0.549		
	Aug/37	0.067	--	1.141		
	1955	0.06	<0.01	0.35	1	Iodine method
		0.17	0.01	1.22		Tot.SO$_4$, alkali trap
Windsor, Ontario	1950,51, 52					Mean monthly values
	Sep	0.092				
	Oct	0.108				
	Nov	0.090				
	Dec	0.147				
	1951,52, 53					
	Jan	0.107				
	Feb	0.116				
	Mar	0.079				
	Apr	0.099				
	May	0.106				
	Jun	0.059				
	Jul	0.093				
	Aug	0.104				
	1951	0.093	0.00	1.454	18	Industrial
		0.006	0.00	0.876		Semi-rural
Yonkers, N.Y.	1936-37	0.032	0.00	0.75	4	
Youngstown, O.	1936-37	0.049	--	0.026	3	15-mi radius of city center
	Oct/36	0.026	--	0.123	2	
	May/37	0.049	--	0.162		

Table A-II

ATMOSPHERIC HYDROGEN SULFIDE CONCENTRATIONS
(ppm by vol)

City	Date	Avg.	Min.	Max.	Ref.	Remarks and Number of Samples
Charleston, W. Va.	Jan-Jun/ 1951	--			7	Central area
		0.007				South area
		0.002				North area
Pittsburgh, Pa. (Oakland area)	Mar-Aug/ 1954				19	
Santa Clara, Calif.	1949-54	--	--	0.9	17	Highest reported value (spotty sampling)
Windsor, Ontario	1950-51?	0.108	--	0.607	20	(49)

Concentration Ranges in % of Time

Conc.	Mar/Apr		May/Jun		Jul/Aug	
0.00	75.2	78.0	65.4	30.3	42.8	44.8
0-0.0025	24.7	15.8	32.3	65.2	54.1	53.1
0.0025-0.005	0.0	6.2	2.2	3.5	2.8	2.0
0.005-0.01	0.0	0.0	0.3	0.9	0.3	0.2
0.01	0.0	0.0	0.0	0.0	0.6	0.0

Table A-III

ATMOSPHERIC NITROGEN OXIDE CONCENTRATIONS EXPRESSED AS NO_2
(ppm by vol)

City	Date	Avg.	Min.	Max.	Ref.	Remarks and Number of Samples
Baltimore, Md.	1950?	0.26	0.05	0.79	4	Downtown (7)
		0.16	0.05	0.54		Industrial (68)
Charleston, W. Va.	1950?	0.12	0.00	0.58	4	(90)
	Jan-Jun/ 1951	0.12			7	Charleston
		0.12				South Charleston
Cincinnati, O.	1949-51	0.23	0.00	0.55	4	(86)
Donora, Pa.	1949	0.15	0.00	0.63	4	(79)
Los Angeles, Calif.	1949-50	<0.10	0.00	0.50	4	
	1950-52	0.02	0.00	0.3	11	
	1953	0.08			12	Clear day-downtown
				0.4		Intense smog-downtown
	Nov 15-20 1954			0.73	17	Avg.max.-high poll.-L.A.
				0.38		" " Pasadena
	Nov 23-28 1954			0.56		" low "L.A.
				0.30		" " Pasadena
	Sep 9/53			1.74	15	Max.to date-central L.A.
San Diego	1949-54	--	--	0.65	17	Highest reported value (spotty sampling)
Santa Clara	1949-54	--	--	0.3	17	" " " (25)
Windsor	1950-51	0.889	0.03	3.48	18	

Table A-IV

ATMOSPHERIC AMMONIA CONCENTRATIONS
(ppm by vol)

City	Date	Avg.	Min.	Max.	Ref.	Remarks and Number of Samples
Baltimore,Md.	1950	0.018	0.005	0.053	4	(6)
Charleston, W. Va.	1950-51	0.04	0.00	0.206	4	(64)
	Jan-Jun/ 1951	0.035			7	Central area
		0.020				South area
		0.017				North area
Chicago,Ill.	1937	0.014			4	
Cincinnati,O.	1949-51	0.023	0.00	0.089	4	(14)
Los Angeles	1950-52	0.1	--	0.2	11	Smoggy day
Salt Lake City	1919	--	>0.001	0.12	4	
Windsor	1950-51	0.216	--	3.07	20	(41)

Table A-V

ATMOSPHERIC ALDEHYDE CONCENTRATIONS EXPRESSED AS FORMALDEHYDE
(ppm by vol)

City	Date	Avg.	Min.	Max.	Ref.	Remarks and Number of Samples
Baltimore,Md.	1950?	0.067	0.025	0.12	4	(4)
Charleston, W. Va.	1950?	0.04	0.00	0.13	4	(134)
	Jan-Jun/ 1951	0.047				Central area
		0.044				South area
		0.041				North area
Cincinnati,O.	1949-51	0.070	0.00	0.27	4	(34)
Los Angeles, Calif.	Oct 14-15 1946		0.11	0.79	21	Heavy smog
	1949-50	<0.18	0.00	1.0	4	
	1950-52	0.02	--	0.03	11	Smoggy day
		0.8		2.0		Aldehydes and ketones as CHO
	1953?	0.07			12	Clear day
		0.40				Intense smog
	1954	0.20			13	
	1955			0.8	15	Max.to date-central L.A.
Louisville,Ky.	1954	0.07	0.00	1.80	22	Western area
San Diego, Calif.	1949-54	--	--	0.62	17	Highest reported value (spotty sampling)
Santa Clara, Calif.	1949-54	--	--	0.6	17	" " " (routine sampling)
Windsor, Ontario	1951-52	0.20	0.00	0.85	18	

Table A-VI

ATMOSPHERIC HYDROCARBON CONCENTRATIONS
(ppm by vol)

City	Date	Avg.	Min.	Max.	Ref.	Remarks and Number of Samples
Los Angeles, Calif.	1949-54			2.09	17	Max.reported value
	1953?	0.2			12	Clear day
	1954	0.38		1.1	13	Intense smog-prelim. value
	Oct 15-20 1954			0.88	17	L.A.-avg.max-high poll
				0.22		Pasadena- " " "
	Oct 23-28 1954			0.23		L.A.- " " low "
				0.15		Pasadena- " " "
Long Beach	1955			3.02	15	Max. conc.
San Diego, Calif.	1949-54	--	--	1.39	17	Highest reported value (spotty sampling)

Table A-VII

ATMOSPHERIC CHLORIDE CONCENTRATIONS
(ppm by vol)

City	Date	Avg.	Min.	Max.	Ref.	Remarks and Number of Samples
Baltimore,Md.	1950	0.037	0.001	0.11	4	(79)
Charleston, W. Va.	1950-51	0.016	0.00	0.068	4	(152)
	Jan-Jun 1951	0.039			7	Charleston
		0.035				South Charleston
		0.027				North Charleston
Chicago,Ill.	1937	0.078			4	
Cincinnati,O.	1946-51	0.033	0.00	0.19	4	All areas (227)
		0.026	0.00	0.106		Rural (52)
		0.030	0.00	0.108		Residential (57)
		0.034	0.00	0.19		Ind. and Comm. (176)
Donora,Pa.	1949	0.071	0.00	0.3	4	(247)
Los Angeles, Calif.	1950	--	--	0.15	4	
Louisville	1954	0.04			22	Western area
Salt Lake City,Utah	1919	--	0.01	0.025	4	
Windsor, Ontario	1950-51	0.095	0.00	0.618	20	(48)

Table A-VIII

ATMOSPHERIC CARBON MONOXIDE CONCENTRATIONS

(ppm by vol)

City	Date	Avg.	Min.	Max.	Ref.	Remarks and Number of Samples
Baltimore, Md.	1950?	10.0	<5	15	4	
Cincinnati, O.	1949-51	<5	0	15	4	Rural (43)
		4.0	0	25		Residential (118)
		9.5	0	55		Comm. & Ind. (212)
		7.5	0	55		All areas (373)
Detroit, Mich.	1952-53	2.0	0.5	3.0	23	Approx. 150 ft elevation (10)
Donora, Pa.	1949	<5.0	0.0		4	(9)
London, England	Dec/52			300	47	Severest fog-indirectly estimated
Los Angeles, Calif.	1949-54			42.9	17	Highest reported value
	1953?	3.5			12	Clear day-downtown
				23.0		Intense smog-downtown
	Oct/54	6.0	1.0	15.0	23	150 ft above ground (157)
	Oct 15-20 1954			2.16	17	L.A.-avg.max.-high poll.
				2.78		Pasadena- " " "
	Oct 23-28 1954			1.27		L.A.- " " low "
				1.88		Pasadena- " " "
	Oct 29 1955			99.0	15	Max. conc. to date - West Los Angeles
San Diego, Calif.	1949-54	--	--	3.3	17	Highest reported value (spotty sampling)
Santa Clara, Calif.	1949-54	--	--	1.2	17	Highest reported value (spotty sampling)

Table A-IX

ATMOSPHERIC OXIDANT CONCENTRATIONS EXPRESSED AS OZONE
(ppm by vol)

City	Date	Avg.	Min.	Max.	Ref.	Remarks and Number of Samples
Akron, O.	1955	0.011	0.002	0.032	1	
Ann Arbor, Mich.	1955	0.047	0.026	0.074	1	
Charleston, W. Va.	1955	0.049	0.012	0.118	1	
Cincinnati, O.	1955	0.033	0.002	0.08	1	
College, Alaska	1950	0.032	0.005	0.24	25	
Detroit, Mich.	May/51	0.026			26	
	Jun 21-28 1951	0.022				(3)
	1955	0.026	0.0	0.055	1	
Elizabeth, N.J.	1955	0.009	0.00	0.028	1	
Los Angeles, Calif.	Mar/49	0.145	0.112	0.193	26	(10)
	Apr/49	0.171	0.144	0.210		(7)
	May/49	0.141	0.092	0.258		(13)
	Jun/49	0.251	0.089	0.437		(22)
	Jul/49	0.305	0.230	0.345		(12)
	Aug/49	0.349	0.177	0.471		(16)
	Sep/49	0.301	0.108	0.286		(18)
	Oct/49	0.248	0.049	0.499		(18)
	Nov/49	0.276	0.222	0.485		(7)
	Dec/49	0.106	0.005	0.318		(16)
	Jan/50	0.111	0.008	0.227		(13)
	Feb/50	0.177	0.044	0.312		(16)
	Mar/50	0.189	0.043	0.333		(24)
	May/51	0.146	0.065	0.182		(9)
	Jun/51	0.145	0.125	0.169		(6)
	Jul/51	0.162	0.145	0.174		(3)
	1950-52	0.3	--	0.6	11	Smoggy day
	1949-54			1.00	17	Highest reported value
	1954			0.42	13	Avg.max.=0.13-L.A.
				0.50		" " 0.17-Pasadena
	Oct 15-20 1954			0.28	17	Avg.max.-L.A. KI method-high pollution
				0.30		" " "-Pasadena
				0.49		Avg.max.-Pasadena. Phenolpthalein method-high pollution

Table A-IX (Cont'd.)

City	Date	Avg.	Min.	Max.	Ref.	Remarks and Number of Samples
Los Angeles, Calif. (cont'd.)	Oct 23-28 1954			0.11		Avg.max.-L.A. KI method-low pollution
				0.19		Avg.max.-Pasadena. KI method-low pollution
				0.16		Avg.max.-Pasadena. Phenolpthalein method low pollution
	Sep 13 1955			0.90	15	Max.conc.-Vernon (LACAPCD)
Philadelphia, Pa.	1955	0.015	0.00	0.05	1	
St.Louis,Mo.	1955	0.027	0.002	0.08	1	
San Diego, Calif.	1949-54	--	--	0.22	17	Highest reported value (spotty sampling)
San Francisco,Calif.	Sep/54-Dec/55				127	"Bay Area"-phenolptha-lin method
	1954					
	Sep	0.067	0.00	0.29		
	Oct	0.080	0.00	0.33		
	Nov	0.046	0.00	0.32		
	Dec	0.033	0.00	0.11		
	1955					
	Jan	0.034	0.00	0.19		
	Feb	0.077	0.00	0.22		
	Mar	0.073	0.01	0.29		
	Apr	0.055	0.00	0.24		
	May	0.073	0.00	0.40		
	Jun	0.055	0.00	0.42		
	Jul	0.055	0.00	0.50		
	Aug	0.063	0.00	0.39		
	Sep	0.071	0.00	0.60		
	Oct	0.069	0.00	0.45		
	Nov	0.067	0.00	0.39		
	Dec	0.026	0.00	0.13		
Santa Clara, Calif.	1949-54	--	--	0.33	17	Highest report value (daily sampling)
Washington, D. C.	1955	0.039	0.003	0.078	1	
	Jun 7/51	0.027			26	O_3 concentration
Whiting,Ind. (Chicago)	1955	0.037	0.00	0.10	1	

Table A-X

ATMOSPHERIC FLUORIDE CONCENTRATIONS EXPRESSED AS HYDROGEN FLUORIDE
(ppm by vol)

City	Date	Avg.	Min.	Max.	Ref.	Remarks and Number of Samples
Baltimore, Md.	1950	0.018	0.00	0.080	4	Industrial (79)
		0.008	0.00	0.021		Residential (21)
Charleston, W. Va.	1950-51	0.003	0.00	0.030	4	(132)
Cincinnati, O.	1946-51	0.005+	0.00	0.025	4	All areas (386)
		0.0047	0.00	0.025		Rural areas (75)
		0.006	0.00	0.025		Residential areas(94)
		0.005	0.00	0.025		Ind. & Comm. (295)
Donora,Pa.	1948-49	0.008	0.00	0.060	4	(40)
	1949	0.006	0.00	>0.030	28	(249)1.7-cu m samples
			0.00	0.006		(16)14.7-cu m samples
Cleveland,O.	1949-50					Industrial area (256)
Los Angeles	Apr/48	0.0077	0.0007	0.0269	4,29	Residential area (20)
Portland,Ore.	1954-56	0.0008	0.00	0.005	30	8-hr samples (239)

Table A-XI

ATMOSPHERIC CARBON DIOXIDE CONCENTRATIONS
(ppm by vol)

City	Date	Avg.	Min.	Max.	Ref.	Remarks and Number of Samples
Berlin, Germany	1926	--	307	402	5	
Chicago,Ill.	1912-13	330			4	
	1926	--	317	374	5	
Cincinnati,O.	1949-51	330	310	390		Rural (18)
		370	300	520		Residential (22)
		390	320	600		Comm. & Ind. (64)
		380	300	600		All areas (86)
Cleveland,O.	1926	--	352	452	5	
London, England	1926	--	345	439	5	
	Dec/52		2000	5000	24	Most severe fog with inversion (indirectly estimated)
Manchester, England	1926	--	311	403	5	
Paris,France	1926	--	243	422	5	
Salt Lake City,Utah	1919-20	335			4	
	1926	--	270	430	5	

Table A-XII

GROSS PARTICULATE LOADING OF THE AIR
(μg/cu m)

City	Date	Avg.	Min.	Max.	Ref.	Remarks and Number of Samples
Anchorage, Alaska	1954	(annual)			13	Staplex high-vol.filter 2000 cu m/24 hr
		308				Tot.air loading-urban
		21.4				Acetone sol.fraction-urban area
				>3000 (abs)		Volcanic ash and summer dust
Atlanta,Ga.	1954	(annual)			13	Staplex high-vol.filter 2000 cu m/24 hr
		137				Tot.air loading-urban
		24.2				Acetone sol.fraction-urban area
		71				Tot.air loading-nonurban
		9.3				Acetone sol.fraction-nonurban area
Baltimore,Md.	1931-33					Selected months
		630(a)			31	Tot.air loading-urban
			510	720	4	" " " "
		430(a)			31	Comb.fraction- "
		200(a)			31	Ash-urban areas
	1950	(annual)			4	Tot.air loading only
		870	210	1720		Downtown area (12)
		380	50	1460		Industrial area (78)
Berlin, Germany	1926		60	310	5	
Boonsboro,Md.	1954	(annual)			13	Staplex high-vol.filter 2000 cu m/24 hr
		68				Tot.air loading-nonurban
		8.7				Acetone sol.fraction-nonurban area
Boston,Mass.	1931-33				31	Selected months
		630(a)				Tot.air loading-urban
		430(a)				Comb.fraction-urban
		200(a)				Ash-urban areas
Buffalo,N.Y.	1931-33				31	Selected months
		520(b)				Tot.air loading-urban
		320(b)				Comb.fraction-urban
		200(b)				Ash-urban area

Table A-XII (Cont'd.)

City	Date	Avg.	Min.	Max.	Ref.	Remarks and Number of Samples
Charleston, W. Va.	1950	260	40	1170	4	Tot.avg.air loading(144)
	Jan6/51	528			7	Tot.air loading-central
		435				" " " -south
		363				" " " -north
	Jul 8/51	339	246	404	7	" " " -central
		246	85	392		" " " -north
		177	79	345		" " " -south
		159	83	265		" " " -south
	1954	(annual)			13	Staplex high-vol.filter 2000 cu m/24 hr
		288				Tot.air loading-urban
		25.4				Acetone sol.fraction-urban area
Chicago, Ill.	1926	--	32	1958	5	Tot. air loading
	1931-33				31	Selected months
		630(a)				Tot. air loading
		430(a)				Combustible fraction
		200(a)				Ash
Cincinnati, O	1946-51				4	Tot. air loading
		370	10	1980		All areas (537)
		280	10	1300		Residential (202)
		420	10	1980		Ind. and comm.(335)
		180	20	450		Rural (79)
	1954				13	Staplex high-vol.filter 2000 cu m/24 hr
		176				Tot.air loading-urban
		34.4				Acetone sol.fraction-urban area
		45				Tot.air loading-non-urban area
		9				Acetone sol.fraction-nonurban area
Cleveland, O.	1926		150	3990	5	Abs.values of tot.air loading
	1931-33				31	Selected months
		520(b)				Tot. air loading
		320(b)				Combustible fraction
		200(b)				Ash
Detroit, Mich	1931-33				31	Selected months
		350(c)				Tot. air loading
		210(c)				Combustible fraction
		140(c)				Ash
	1951				8	6-wk period during May and Jun
		295	95	730		Comm. and Ind.
		172	45	394		Residential

Table A-XII (Cont'd.)

City	Date	Avg.	Min.	Max.	Ref.	Remarks and Number of Samples
Detroit, Mich. (cont'd.)	1952				8	6-wk period during Aug and Sep
		293	102	580		Comm. and ind.
		184	33	580		Residential
	1951				9	6-wk period during Oct and Nov
		210	36	467		High atmos.pressure
		150	1	556		Medium " "
		80	3	214		Low " "
	1952	247	27	718	9	High " "
		170	22	568		Medium " "
		107	3	257		Low " "
Donora, Pa.	1948-49	700	260	1900	4	(28)
	1949	740	Nil	2500	4	(205)
Fort Wayne, Ind.	1954	(annual)			13	Staplex high-vol.filter 2000 cu m/24 hr
		110				Tot. air loading
		14				Acetone sol. fraction
Hamburg, Germany	1926	30	150		5	Total air loading
Houston, Tex.	1954	(annual)			13	Staplex high-vol.filter 2000 cu m/24 hr
		129				Tot. air loading
		18.5				Acetone sol.fraction
Kansas City, Mo.	1954	(annual)			13	Staplex high-vol.filter 2000 cu m/24 hr
		146				Total air loading
		18.4				Acetone sol.fraction
London, England	Nov/48				10	During 6 days of severe fog
		1190	--	1780		Mean of central sites
		490	--	740		" " outer "
	Dec/51		120	490		Greater London
	Dec/52	1980	--	2650		Mean of central sites
		1000	--	1510		" " outer "
			30	4460		Abs.values for Greater London
Los Angeles, Calif.	1931-33				31	Selected months
		350(c)				Tot. air loadings
		210(c)				Combustible fraction
		140(c)				Ash
	1949-54			1222	17	Abs.tot.air loading
				411		Abs. comb.fraction
				254		Organic particulate
	1954	(annual)			13	Staplex high-vol.filter 2000 cu m/24 hr

Table A-XII (Cont'd.)

City	Date	Avg.	Min.	Max.	Ref.	Remarks and Number of Samples
Los Angeles (cont'd)		265				Tot.air loading
		57				Acetone sol.fraction
	Oct/54				17	5-day period during each pollution level
				477		Avg.-high poll.-L.A.
				306		" " " -Pasadena
				414		" low " -L.A.
				278		" " " -Pasadena
(See also Supplementary Tabulation for Los Angeles at end of this table)						
Louisville, Ky.	1954	(annual)			13	Staplex high-vol.filter 2000 cu m/24 hr
		184				Tot. air loading
		18.3				Acetone sol. fraction
Minneapolis, Minn.	1954	(annual)			13	Staplex high-vol.filter 2000 cu m/24 hr
		120				Tot. air loading
		15.8				Acetone sol. fraction
New Orleans, La.	1931-33				31	Selected months
		520(b)				Tot. air loading
		320(b)				Combustible fraction
		200(b)				Ash
New York, N.Y.	1931-33				31	Selected months
		520(b)				Tot. air loading
		320(b)				Combustible fraction
		200(b)				Ash
	1954	(annual)			13	Staplex filter
		244				Tot. air loading
		38				Acetone sol.fraction
(See also Supplementary Tabulation for Pasadena at end of this table)						
Philadelphia, Pa.	1931-33				31	Selected months
		520(b)				Tot. air loading
		320(b)				Combustible fraction
		200(b)				Ash
	1954	(annual)			13	Staplex filter
		188				Tot. air loading
		30				Acetone sol.fraction
Pittsburgh, Pa.	1931-33				31	Selected months
		630(a)				Tot. air loading
		430(a)				Combustible solids
		200(a)				Ash

Table A-XII (Cont'd.)

City	Date	Avg.	Min.	Max.	Ref.	Remarks and Number of Samples
Portland, Ore.	1954	(annual)			13	Staplex filter
		143				Tot.air loading-urban
		32				Acetone sol.fraction-"
		86				Tot.air load.-nonurban
		12.4				Acetone sol.fraction-"
St.Louis, Mo.	1931-33				31	Selected months
		630(a)				Tot. air loading
		430(a)				Combustible solids
		200(a)				Ash
Salt Lake City, Utah	1926		Nil	2500		Tot.air loading
	1954	(annual)			13	Staplex filter
		55				Tot. air loading
		6.2				Acetone sol.fraction
San Francisco	1931-33				31	Selected months
		350(c)				Tot. air loading
		210(c)				Combustible solids
		140(c)				Ash
	1949-54			298	17	Tot.air loading-abs.
				69.5		Organic part.- "
	1954	(annual)			13	Staplex filter
		104				Tot. air loading
		19.4				Acetone sol. fraction
Santa Clara, Calif.	1949-54				17	Highest reported values
				400		Tot. air loading
				43.6		Organic particulate
Washington, D. C.	1931-33				31	Selected months
		350(c)				Tot. air loading
		210(c)				Combustible solids
		140(c)				Ash
	1954	130			32	Tot. air loading
		27.3				Acetone sol. fraction
Windsor, Ontario	Oct-Dec 1951					Tot. air loading
		210	36	470		High pollution area
		150	1	560		Medium " "
		80	3	210		Low " "

(a) Average of a group of cities which include Baltimore, Boston, Chicago, Pittsburgh, St. Louis.

(b) Average of a group of cities which include Buffalo, Cleveland, New Orleans, New York, Philadelphia.

(c) Average of a group of cities which include Detroit, Los Angeles, San Francisco, Washington, D. C.

Supplementary Tabulation

GROSS PARTICULATE LOADING OF THE AIR
(μg/cu m)

City	Date	Avg.	Min.	Max.	Ref.	Remarks and Number of Samples
Los Angeles, Calif.	Aug-Nov 1954	385			14	4-mo avg. total loading (111)
			145			Abs. values in 111 samples
				1220		" " " "
Pasadena, Calif.	Aug-Nov 1954	256			14	4-mo avg. total loading (111)
			15			Abs. values in 111 samples
				660		" " " "

City	Date	Ref.	Ag	Al	As	Ba	Be	Bi	Ca	Cd	Cr	Cu	F^-	Fe	Fe_xO_y	Hg	K	M
Anchorage,Alaska	1954	13			< 0.01		0.0001					0.06	-	8.5				
Atlanta,Georgia	1954	13			< 0.01		0.0002					0.01	0.05	3.3				
	1954	13			0.01		0.0002					< 0.01	Nil	2.7				
Baltimore,Maryland	1931-33	31													13(a)			
	1950	4	0.10	4.0			< 0.0005			< 0.2		0.40		15.1				
Boonsboro,Maryland	1954	13			0.01		0.0001					Nil	-	3.7				
Boston,Massachusetts	1931-33	31													13(a)			
Buffalo,New York	1931-33	31													11(b)			
Charleston,West Virginia	1950	4	<0.02	8.6	<0.10	<0.2	0.0003		3.4			0.60	0.5	4.4		0.07	<10.0	<10.0
	Jul-Aug/51	7		1.3		0.01	< 0.003		1.2	Nil	Trace	0.97		0.19				0.2
	Jul-Aug/51	7		1.97		0.01	< 0.002		0.99	0.002	Trace	0.01		0.99				0.2
	1954	13			0.09		0.0003					0.04	Nil	5.30				
Chicago,Illinois	1931-33	31													13(a)			
	1954	13			0.04		0.0002					0.11	0.03	7.90				
Cincinnati,Ohio	1946-51	4																
	1946-51	4																
	1946-51	4																
	1946-51	4																
	1946-51	4	<0.10	4.4	0.06		0.0095		16.0	0.22		0.86	0.93	12.50		0.10	48.0	< 7.0
	1946-51	4	<0.10	0.1			0.0001(d)		0.4	< 0.10		0.01	0.10	0.10		0.03	< 3.0	< 5.0
	1946-51	4	0.80	25.0	0.06		0.060(d)		65.0	0.42		32.0	2.90	110.0		0.21	230.0	<10.0
	1946-51	4	<0.10	1.9	-		0.003		9.0	-		0.88	0.67	5.7		-	20.0	<10.0
Cleveland,Ohio	1931-33	31													11(b)			
Detroit,Michigan	1931-33	31													10(c)			
	May-Jun/51	8		2.9		0.02	Trace		2.1	0.003	0.01	0.09		3.1				0.9
	May-Jun/51	8		Trace		Nil	Nil			Nil	Nil	0.008		Nil				0.0
	May-Jun/51	8		17.4		0.20	0.01			0.07	0.20	2.60		20.7				5.2
	Aug-Sep/52	8		3.6		0.02	Nil	0.02		Trace	0.02	0.08		2.4				0.9
	Aug-Sep/52	8		0.4		Trace	Nil	Nil		Nil	Trace	Nil		Trace				0.3
	Aug-Sep/52	8		29.9		0.04	0.010	0.04		0.04	0.30	1.20		15.6				4.5
	1954	13			0.04		0.004					0.57	0.04	8.3				
Donora,Pennsylvania	1948-49	4	<0.10	6.0						0.80		1.00		14.0				
Fort Wayne,Indiana	1954	13			0.01		0.0001					0.31	0.01	3.6				
Houston,Texas	1954	13			0.01		0.0002					0.02	Nil	4.0				
Kansas City,Missouri	1954	13			0.02		0.0003					0.04	0.01	4.1				
Los Angeles,California	1931-33	31													10(c)			
	1950	4		2.5		0.10			2.5			0.10		2.5				1.1
	1950	4		6.0		0.24			2.5			0.24		6.0				2.5
	1949-54	17	0.0027	8.0	0.65		0.002		7.0			1.40	65.0	18.3			7.2	19.6
	1954	13			0.20		0.0001					0.13	0.38	4.7				
	1954	14	<0.001		0.01		0.0002					0.36	0.94	5.04			3.4	6.3
	1954	14	Nil		Nil		<0.0001					0.02	Nil	1.3			0.1	Nil
	1954	14	0.0016		0.04		0.0007					1.32	6.30	22.0			7.2	13.7
Louisville,Kentucky	1954	13			0.02		0.0004					0.16	Nil	6.6				
Minneapolis,Minnesota	1954	13			0.01		0.0002					0.60	0.06	4.4				
New Orleans,Louisiana	1931-33	31													11(b)			
New York,New York	1931-33	31													11(b)			
	1954	13			0.05		0.0003					0.30	0.21	5.2				
Pasadena,California	1954	14	<0.001		0.01		0.0002					0.17	0.42	3.02			2.7	4.9
	1954	14	Nil		Nil		<0.0001					0.01	Nil	Nil			0.3	Nil
	1954	14	0.0018		0.04		0.0005					1.40	1.6	11.5			6.6	16.4
Philadelphia,Pennsylvania	1931-33	31													11(b)			
	1954	13			0.16		0.0005					1.34	0.24	6.5				
Pittsburgh,Pennsylvania	1931-33	31													13(a)			
Portland,Oregon	1954	13			0.02		0.0003					0.05	Nil	5.1				
	1954	13			0.04		0.0001					<0.01	-	3.6				
St.Louis,Missouri	1931-33	31													13(a)			
Salt Lake City,Utah	1954	13			0.03		< 0.0001					0.28	-	4.1				
San Francisco,California	1931-33	31													11(c)			
	1949-54	17	<0.0008		0.07		0.0003					0.296		5.2			2.52	6.0
	1954	13			0.01		0.0001					0.07	0.37	2.4				
Santa Clara,California	1949-54	17	<0.0009		0.03		0.0004					0.61		6.4			2.5	6.9
Washington,D.C.	1931-33	31													11(c)			
Windsor,Ontario	1951	18		2.75		0.03	0.006		3.26	0.01	0.01	0.25		2.49				0.8
	1951	18		0.71		Nil	Nil		0.85	0.00+	Nil	0.01		0.59				0.2
	1951	18		6.94		0.18	0.073		13.88	0.05	0.04	0.83		8.77				2.6

(a) Average of a group of cities which include Baltimore, Boston, Chicago, Pittsburg, and St. Louis.
(b) Average of a group of cities which include Buffalo, Cleveland, New Orleans, New York, and Philadelphia.
(c) Average of a group of cities which include Detroit, Los Angeles, San Francisco, and Washington.
(d) Uncertain values

SPECI

	Bi	Ca	Cd	Cr	Cu	F^-	Fe	Fe_xO_y	Hg	K	Mg	Mn	Na	Ni	NO_3^-	Pb	S	SiO_2	Sn	SO_4^{--}	Ti	V	
001					0.06	-	8.5					0.20			-	1.20			< 0.01	5.4	1.060	0.007	
002					0.01	0.05	3.3					0.12			0.8	1.80			0.03	1.0	0.120	0.024	
002					< 0.01	Nil	2.7					0.11			-	0.90			< 0.01	0.5	0.130	0.004	
								13(a)									84(a)	77(a)					
05			< 0.2		0.40		15.1					0.3				1.00		30.5	< 0.20		0.500	0.200	
001					Nil	-	3.7					Nil			-	0.10			< 0.01	0.3	0.260	0.003	
								13(a)									84(a)	77(a)					
								11(b)									81(b)	58(b)					
003		3.4			0.60	0.5	4.4		0.07	< 10.0	< 10.0	0.3	< 40.0			0.60			< 0.20	9.0	0.400	0.020	
3		1.2	Nil	Trace	0.97		0.19				0.26	0.13		Nil		0.65		42.5	0.07		0.007	Nil	
2		0.99	0.002	Trace	0.01		0.99				0.25	0.10		Nil		0.12		32.3	0.007		Trace	Nil	
003					0.04	Nil	5.30					0.19			1.1	1.10			< 0.01	7.3	0.240	0.005	
								13(a)									84(a)	77(a)					
002					0.11	0.03	7.90					0.11			1.7	2.80			0.03	9.4	0.180	0.002	
																1.10							
																1.94							
																3.50							
																2.70							
95		16.0	0.22		0.86	0.93	12.50		0.10	48.0	< 7.0	0.30	28.0			2.70			< 0.20	1.9	< 1.00	< 0.2	
01(d)		0.4	< 0.10		0.01	0.10	0.10		0.03	< 3.0	< 5.0	0.00+	< 10.0			< 0.10			< 0.01	0.1	< 0.10	0.2	
0(d)		65.0	0.42		32.0	2.90	110.0		0.21	230.0	< 10.0	2.00	84.0			11.50			12.00	8.5	20.00	0.4	
3		9.0	-		0.88	0.67	5.7		-	20.0	< 10.0	0.20	< 20.0			1.20			< 0.20		< 1.00	< 0.2	
								11(b)									81(b)	58(b)					
								10(c)									49(c)	45(a)					
		2.1	0.003	0.01	0.09		3.1				0.9	0.20		0.01		0.70		14.5	0.04		0.05	0.003	
			Nil	Nil	0.008		Nil				0.02	0.01		Nil		Nil		1.75	Nil		Nil	Nil	
			0.07	0.20	2.60		20.7				5.2	0.60		0.30		3.9		52.5	0.20		0.40	0.04	
	0.02		Trace	0.02	0.08		2.4				0.9	0.20		0.009		0.4		16.6	0.04		0.06	0.008	0.
	Nil		Nil	Trace	Nil		Trace				0.3	0.03		Nil		0.01		0.9	Trace		Nil	Nil	Ni
0	0.04		0.04	0.30	1.20		15.6				4.5	0.50		0.03		1.60		32.6	0.08		1.50	0.020	0.
4					0.57	0.04	8.3					0.74			1.2	2.9			0.06	7.5	0.028	0.025	
			0.80		1.00		14.0					0.60				4.5			< 0.20				
01					0.31	0.01	3.6					0.05			1.1	0.8			< 0.01	1.1	0.02	0.004	
02					0.02	Nil	4.0					0.23			1.0	1.0			0.02	2.4	0.29	0.001	
03					0.04	0.01	4.1					0.08			0.6	1.0			0.03	1.5	0.21	0.002	
								10(c)									49(c)	45(c)					
		2.5			0.10		2.5				1.1					0.8							
		2.5			0.24		6.0				2.5					6.0							
3		7.0			1.40	65.0	18.3			7.2	19.6	1.86	8.6		116.0	42.0		85.2	0.96	154.5	1.02	0.169	
01					0.13	0.38	4.7					0.15			14.4	5.2			0.02	14.4	0.30	0.002	
02					0.36	0.94	5.04			3.4	6.33	0.18	5.5		24.3	6.53			0.03	27.3	0.19	0.029	
01					0.02	Nil	1.3			0.1	Nil	0.09	1.2		0.4	1.40			< 0.01	0.2	0.01	Nil	
07					1.32	6.30	22.0			7.2	13.70	0.40	10.1		116.0	16.40			0.96	154.5	0.65	0.097	
04					0.16	Nil	6.6					0.09			1.5	0.6			0.02	0.06		0.001	
02					0.60	0.06	4.4					0.08			1.3	0.5			0.01	0.8	0.11	0.002	
								11(b)									81(b)	58(b)					
								11(b)									81(b)	58(b)					
03					0.30	0.21	5.2					0.07			0.8	2.8			0.08	14.8	0.41	0.322	
02					0.17	0.42	3.02			2.7	4.9	0.13	3.8		15.5	4.07			< 0.01	16.9	0.14	0.021	
01					0.01	Nil	Nil			0.3	Nil	0.01	Nil		0.6	0.80			Nil	Nil	0.01	Nil	
5					1.40	1.6	11.5			6.6	16.4	0.40	6.6		107.0	12.80			0.06	125.3	0.94	0.033	
								11(b)									81(b)	58(b)					
5					1.34	0.24	6.5					0.54			1.6	9.5			0.16	15.6	0.15	0.175	
								13(a)									84(a)	77(a)					
03					0.05	Nil	5.1					0.23			0.2	1.2			0.01	0.8	0.24	0.009	
1					< 0.01	-	3.6					0.04			-	0.3			0.01	0.4	Nil	0.002	
								13(a)									84(a)	77(a)					
1					0.28	-	4.1					0.04				0.10				< 0.01	Nil	Nil	
								11(c)									49(c)	45(c)					
3					0.296		5.2			2.52	6.0	0.12	7.4			3.5			0.05	25.0	0.21	0.013	
1					0.07	0.37	2.4					0.11			3.4	2.4			0.02	1.8	0.04	0.002	
4					0.61		6.4			2.5	6.9	0.05	4.9			0.9			< 0.01	4.65	0.24	0.014	
								11(c)									49(c)	45(c)					
		3.26	0.01	0.01	0.25		2.49				0.81	0.28		0.03		0.61		18.1	0.05		0.07	0.017	
		0.85	0.00+	Nil	0.01		0.59				0.20	0.06		0.01		0.13		3.2	0.01		0.01	Nil	
		13.88	0.05	0.04	0.83		8.77				2.64	0.91		0.07		1.81		63.5	0.11		0.18	0.280	

sburg, and St. Louis.
, New York, and Philadelphia.
isco, and Washington.

Table A-XIII

SPECIFIC CHEMICAL PARTICULATE LOADING OF THE AIR FOR VARIOUS CITIES
(Micrograms/cu m)

	Ni	NO_3^-	Pb	S	SiO_2	Sn	SO_4^{--}	Ti	V	W	Zn	Remarks
		-	1.20			< 0.01	5.4	1.060	0.007			Annual average values
		0.8	1.80			0.03	1.0	0.120	0.024			Annual averages for urban areas
		-	0.90			< 0.01	0.5	0.130	0.004			Annual averages for nonurban areas
				84(a)	77(a)							Average values for selected periods
			1.00		30.5	< 0.20		0.500	0.200			Average values for industrial areas
		-	0.10			< 0.01	0.3	0.260	0.003			Average values for nonurban areas
				84(a)	77(a)							Average values for selected periods
				81(b)	58(b)							Average values for selected periods
.0			0.60			< 0.20	9.0	0.400	0.020		1.6	Annual average for urban area (Cl^-=2.5)
	Nil		0.65		42.5	0.07		0.007	Nil			Average value for urban area (Mo=0.01)
	Nil		0.12		32.3	0.007		Trace	Nil			Average value for north area (Mo=0.01)
		1.1	1.10			< 0.01	7.3	0.240	0.005			Average value for urban area
				84(a)	77(a)							Average value for selected periods
		1.7	2.80			0.03	9.4	0.180	0.002			Annual average for urban area
			1.10									5 yr average annual value for rural
			1.94									5 yr average annual value for residential
			3.50									5 yr average annual value for industrial-commercial
			2.70									5 yr average annual value for all areas
.0			2.70			< 0.20	1.9	< 1.00	< 0.2		2.0	5 yr average all areas (Sb= 0.2,Cl^-=1.9)
.0			< 0.10			< 0.01	0.1	< 0.10	0.2		0.1	5 yr average minimum all areas (Cl^-=0.24)
.0			11.50			12.00	8.5	20.00	0.4		14.0	Maximum values all areas (Sb= 0.2, Cl^-=6.6)
.0			1.20			< 0.20		< 1.00	< 0.2		1.6	Average values rural areas
				81(b)	58(b)							Average values for selected periods
				49(c)	45(a)							Average values for selected periods
	0.01		0.70		14.5	0.04		0.05	0.003		0.3	6 wk average values all areas (Mo=0.01)
	Nil		Nil		1.75	Nil		Nil	Nil		Nil	6 wk average minimum values all areas (Mo=trace)
	0.30		3.9		52.5	0.20		0.40	0.04		3.9	6 wk average maximum all areas (Sb=0.06,Co=0.02)
	0.009		0.4		16.6	0.04		0.06	0.008	0.009	0.2	6 wk average all areas (Mo=0.04,Sb=tr,Co=nil)
	Nil		0.01		0.9	Trace		Nil	Nil	Nil	Nil	6 wk average minimum all areas (Mo,Sb,Co,=trace)
	0.03		1.60		32.6	0.08		1.50	0.020	0.30	1.5	6 wk average maximum all areas (Mo=0.09,Sb=0.03,Co=0.004)
		1.2	2.9			0.06	7.5	0.028	0.025			Annual average for urban areas
			4.5			< 0.20					34	Short period average values
		1.1	0.8			< 0.01	1.1	0.02	0.004			Annual average for urban areas
		1.0	1.0			0.02	2.4	0.29	0.001			Annual average for urban areas
		0.6	1.0			0.03	1.5	0.21	0.002			Annual average for urban areas
				49(c)	45(c)							Average value for selected periods
			0.8									Average minimum values
			6.0									Average maximum values
.6		116.0	42.0		85.2	0.96	154.5	1.02	0.169			Highest reptd values(org.partic.=254,polycyc.HC=24.6-33.5,H_2SO_4=110,Sr=1.08)
		14.4	5.2			0.02	14.4	0.30	0.002			Annual average for urban areas
.5		24.3	6.53			0.03	27.3	0.19	0.029			4 mo average values (Sr=0.09,polycyc.HC=8.1,PO_4=1.2)
.2		0.4	1.40			< 0.01	0.2	0.01	Nil			Absolute minimum values (Sr=nil,polycyc.HC=5.1,PO_4=nil,Cl^-=0.2)
.1		116.0	16.40			0.96	154.5	0.65	0.097			Absolute maximum values (Sr=0.28,polycyc.HC=33.5,PO_4=4.7,Cl^-=5.1)
		1.5	0.6			0.02	0.06		0.001			Annual average for urban areas
		1.3	0.5			0.01	0.8	0.11	0.002			Annual average for urban areas
				81(b)	58(b)							Average values for selected periods
				81(b)	58(b)							Average values for selected periods
		0.8	2.8			0.08	14.8	0.41	0.322			Annual average for urban areas
.8		15.5	4.07			< 0.01	16.9	0.14	0.021			4 mo average values (Sr=0.06,polycyc.H.C.=3.8,PO_4=0.9,Cl^-=0.8)
1		0.6	0.80			Nil	Nil	0.01	Nil			Absolute minimum values (Sr=nil,polycyc.H.C.=0.6, PO_4=nil,Cl^-=nil)
.6		107.0	12.80			0.06	125.3	0.94	0.033			Absolute maximum values (Sr=0.23,polycyc.H.C.=12.9,PO_4=2.7,Cl^-=2.3)
				81(b)	58(b)							Average values for selected periods
		1.6	9.5			0.16	15.6	0.15	0.175			Annual average for urban areas
				84(a)	77(a)							Average values for selected periods
		0.2	1.2			0.01	0.8	0.24	0.009			Annual average for urban areas
		-	0.3			0.01	0.4	Nil	0.002			Annual average for nonurban areas
				84(a)	77(a)							Average values for selected periods
			0.10				< 0.01	Nil	Nil			Annual average for urban areas
				49(c)	45(c)							Average values for selected periods
4			3.5			0.05	25.0	0.21	0.013		0.02	Highest reported values (org.part.=69.5,Sr=0.16)
		3.4	2.4			0.02	1.8	0.04	0.002			Annual average for urban areas
.9			0.9			< 0.01	4.65	0.24	0.014		0.47	Highest reported values (org.part.=43.6,Sr=0.05)
				49(c)	45(c)							Average values for selected periods
	0.03		0.61		18.1	0.05		0.07	0.017		0.20	Annual average for urban areas (Mo=0.03)
	0.01		0.13		3.2	0.01		0.01	Nil		Nil	Annual average minimum for urban areas (Mo=tr)
	0.07		1.81		63.5	0.11		0.18	0.280		0.89	Annual average maximum for urban areas (Mo=0.09)

Table A-XIV

DUSTFALL MEASUREMENTS
(tons/sq mi/month)

City	Date	Avg.	Min.	Max.	Ref.	Remarks
Baltimore, Md.	1928-29	150			22	Downtown (45% ash)
		67				3 mi from center
		28				10 mi from center
Pirmingham, England	1939-44	27.8			18	Insoluble only
Bristol, England	1939-44	11.6			18	Insoluble only
Charlston, W. Va.	1946	78			6	
	1948		20	98	22	67.7-68.1% ash
Chicago, Ill.	1934	96.4	66.9	156.8	1	
	1934-35	67.5	39.1	127.0		
	1935-36	81.2	46.3	118.2		
	1936-37	83.6	52.4	144.0		
	1937-38	65.4	50.7	82.1		
	1938-39	65.8	45.1	83.7		
	1939-40	54.1	36.5	69.0		
	1940-41	55.4	42.0	84.2		
	1941-42	57.0	44.4	83.2		
	1942-43	73.7	60.2	85.0		72.3% ash
	1943-44	73.6	52.5	102.9		73.3% ash
	1944-45	67.7	50.9	113.7		75.4% ash
	1945-46	65.2	53.9	76.2		77.0% ash
	1946-47	61.3	50.5	99.2		80.6% ash
	1943	74.8			33	72.4% ash
	1944	73.6				73.3% ash
	1945	68.1				75.3% ash
	1946	65.2				77.0% ash
	1947	61.2				80.6% ash
	1948	56.2				81.4% ash
	1943	74.8			18	62.3% ash
	1949	57.8				81.0% ash
	1944	66.5	25.5	193.5	34	22 stations-various locations in city
	1945	67.7	25.3	183.7		
Cincinnati, O.	1930-31	54.2			35	
	1932	34.5				
	1933	25.8				
	1934	33.3				
	1935	33.1				
	1936	38.2				
	1937	40.2				
	1938	34.8				
	1939	25.7				
	1940	27.0				
	1941	27.5				

Table A-XIV (Cont'd.)

City	Date	Avg.	Min.	Max.	Ref.	Remarks
Cincinnati, O. (cont'd.)	1942	30.1				
	1943	29.6				
	1944	41.3				
	1945	41.6				
	1946	37.7				
	1942	31			6	
	1943	32				
	1944	35				
	1946	34				
	1948-49	30				
	1949-50	29				
Cleveland, O.	1927-29	66			6	71% ash
	1946	52				
	1949	38				
	1950	36				
Crafton, W.Va.	1922	156			22	53.5% ash
Detroit, Mich.	1927	99			6	
	1945	57				
	1946	51.7				
	1950	59.8				
	1951	62.1				
	1952	64.1				
	1953	72.1				
Glasgow, Scotland	1926	110			5	English tons
	1939-44	29.6			18	Insol.deposited material (East Glasgow)
Crafton, W.Va.	1922	156			6	
Hamburg, Germany	1926	--	29	57.5	5	
Holyoke, Mass.	1949	Winter	Spring	Summer	36	
		100	57	31		Res.-near industry
		33	16	15		City residential
		15	16	10		Suburban (Amhurst)
Leeds, England	1926	--	2	45	5	Total sootfall (English tons)
	1939-44	35.9			18	Insol.deposited material
London, England	1926	--	4.83	35.5	5	Tot.sootfall (English tons)
	1939-44	29.1			18	Insol.deposited material
Los Angeles, Calif.	1946	27.7	21.2	38.5		Tot.dustfall-monthly
	1948	33.3			18	Insol.deposited material

Table A-XIV (Cont'd.)

City	Date	Avg.	Min.	Max.	Ref.	Remarks
Louisville, Ky.	1954	32.4			22	% Ash % Ign. Loss
	Sep/52	39.4				72.8 27.2
	Oct/52	29.8				78.5 21.5
	Nov/52	33.5				76.1 23.9
	Dec/52	--				Lost --
	Jan/53	--				Lost --
	Feb/53	34.7				71.6 28.4
	Mar/53	27.2				70.8 29.2
	Apr/53	37.0				75.1 24.9
	May/53	31.8				70.6 29.4
	Jun/53	26.5				74.1 25.9
	Jul/53	21.6				72.6 27.4
		31.3				73.6 26.4
Manchester, England	1926	20			5	Averages(English tons)
	1939-44	42.9			18	
Milwaukee, Wisc.	1952	Winter	Spring	Summer	36	
		35	34	32		Residential-near ind.
		21	24	21		City residential
		12	15	15		Suburban
New Haven, Conn.	1952	Winter	Spring	Summer	36	(8 months)
		27	23	13		City residential
		21	18	13		Commercial district
		19	19	10		City res.-west
		16	14	12		City res.-east
		18	12	7		Suburban
New York, N.Y.	1936	55			6	
	Apr-Dec 1936	52			37	
	1953	67.5			9	
Philadelphia, Pa.	1934	41			6	
Pittsburgh, Pa.	1912-13	86			22	69.1% ash
	1923-51				6	
	1923	120				
	1929	86				
	1938	60				
	1948	54				
	1950	50				
	1951	46				
	1926		49.66	150.58	5	
	1949	79.0			38	
		75.8				
		33.8				
		35.8				
		44.2				
		40.2				

Table A-XIV (Cont'd.)

City	Date	Avg.	Min.	Max.	Ref.	Remarks
Pittsburgh, Pa.(cont'd.)	1949	61.6				
		65.3				
		35.9				
		25.3				
		37.5				
		39.8				
		71.4				
		64.0				
	1951	45.7			9	
	1954	47.6			39	12 stations
	Jan	66.1				
	Feb	65.1				
	Mar	53.8				
	Apr	47.3				
	May	48.4				
	Jun	60.3				
	Jul	26.7				
	Aug	36.4				
	Sep	33.6				
	Oct	41.9				
	Nov	43.8				
	Dec	48.0				
	1955	48.9				
	Jan	40.9				
	Feb	50.9				
	Mar	59.1				
	Apr	58.4				
	May	34.9				
	Jun	36.3				
	Jul	37.5				
	Aug	34.3				
	Sep	54.5				
	Oct	57.0				
	Nov	64.4				
	Dec	58.9				
	1954-55	47.6	9.2	291.5		12 stations
		48.9				
Rochester, N.Y.	1937	--	12	54	1	12 dust jars
	1938	--	18	42		Heating month's deposit
	1939	--	15	47		2 non-heating months
	1940	--	18	54		
	1941	--	17	38		
	1942	--	17	38		
	1941	27			6	
	1942	25				
	1942	26.4			9	
St.Louis,Mo.	1929	190			6	

Table A-XIV (Cont'd.)

City	Date	Avg.	Min.	Max.	Ref.	Remarks
Salt Lake City, Utah	1919-20	29			22	65.1% ash
	1926	--	1.25	81.67	5	
Seattle, Wash.	1951			9-12	36	Winter
				12-16		Spring
				5-10		Summer
Toronto, Ontario	1932-36	29.8			40	2-4 yr avg.
		50.8				
		28.4				
		11.1				
	1947		31.7	54.2	18	
Washington, D. C.	1932-33	24.3			31	
		25			6	
Windsor, Ontario	Aug-Dec 1951	92.2			20	Heavy poll. area
		53.9				Heavy to med. poll
		42.7				Mod. to low poll.
		35.9				Low pollution
Wyandotte, Mich.	1952	Res.-near Ind.		City-Res.		
		36		20		Winter
		47		36		Spring
		37		23		Summer

Appendix A

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Appendix B

CALCULATED AIR POLLUTANT EMISSIONS FROM CENTERS OF POPULATION

The daily emission of air pollutants from centers of population was calculated for seven United States cities based upon the type and extent of industrial and public activities. The metropolitan areas chosen for this research were Los Angeles, Portland (Oregon), New York, Chicago, San Francisco, Cincinnati, and Louisville.

Using as a basis the weight of air pollutants emitted from all sources, it was possible to calculate an atmospheric concentration of each component, assuming certain topographical and meteorological conditions.

Included in Appendix B is an outline of the approach used to calculate the weight of emissions from centers of populations, as well as pertinent data and summarizing tables and figures.

The calculation of air pollutant emissions from various cities was made because the literature data on measured air concentrations of these substances were both meager and incomplete. Data were meager in that particular emphasis had been placed upon sulfur dioxide and solids or particulate matter by the majority of workers in the field; such data, for example, could not be used to determine a trend in sulfur dioxide concentration with population. The data were incomplete in that "average" concentrations are only the averaged value for the number of test stations scattered throughout the area, and consequently should not be considered as a true average concentration throughout the area. From such data it would be virtually impossible to evaluate an air pollutant concentration against the type and extent of industrial activities.

The present method of calculating the weight of emissions from all sources and finally calculating air concentrations was undertaken to remedy the above objections to the evaluation of measured air concentrations. It should be emphasized strongly that to the writers' knowledge, the present method of calculations has not been attempted previously. The usual result of every initial effort of this kind was encountered; insufficient information was available for an accurate appraisal of the problem presented. The method of assessment does present, however, air pollution on a relative basis. It was also believed that refinement of the prime data would lead to an accurate appraisal of air pollution problems.

I Required Data for Calculation of Emissions

The industrial and public emissions of air pollutants were based upon the energy requirements of particular operations, in addition to a knowledge of the type and amount of emissions from such operations obtained from past experience. Wherever possible, literature data were used to augment the emission data collected by Stanford Research Institute.

Table B-I lists the 1954 daily fuel consumption for the metropolitan areas included in this study. These data were partly prepared by the Economics Division of Stanford Research Institute from various source materials, including Petroleum Facts and Figures and American Petroleum Institute and Bureau of Mines publications. The breakdown of the industrial fuel consumption projected 1947 data to 1954.

Table B-II shows the total energy consumption of industrial activities for the same areas. From the latter table, it is clear that, for example, the petroleum industry in San Francisco and Los Angeles consumed the most energy of all industrial categories. For New York and Chicago the primary industrial category, according to the energy consumed, is the primary metals industry.

Data in Table B-I and B-II, together with the population of the standard metropolitan area (Table B-III) and a knowledge of the type and amount of emissions, are the raw data needed to calculate the weight of air pollutant emissions from industrial and public sources. Data for New York and Chicago are treated in detail as an example of the general method.

II Emissions from Public Activities

Tables B-IV and B-XII contain the weight of the designated air pollutants from various types of public activities. Each table contains a list of the weight and type of emissions for a particular unit operation. The basic data were based upon work completed by Stanford Research Institute supplemented, where possible, by the results of other workers in the field.

Tables B-IV to B-XII illustrate the general method of procedure. Where possible, the emission data collected by Stanford Research Institute were utilized. In certain cases where no basic emission data were available, for example from "Commercial Incinerators," the emission data from a similar type of operation were utilized -- in this case that for "Municipal Incinerators."

Whenever possible, the actual weight of materials burned was obtained. Where such information was not readily available, population was used as an index of weight of material consumed daily.

The organic emissions from the operation of automobiles in New York and Chicago were 2600 and 1500 tons daily, respectively, compared with

Table B-I

INDUSTRIAL AND PUBLIC FUELS USED DAILY IN VARIOUS CITIES 1954

Classification	Los Angeles			Portland			Chicago			New York			San Francisco			Cincinnati			Louisville		
	Coal (1000 tons)	Oil (1000 bbls)	Gas (10^6 cu ft)	Coal (1000 tons)	Oil (1000 bbls)	Gas (10^6 cu ft)	Coal (1000 tons)	Oil (1000 bbls)	Gas (10^6 cu ft)	Coal (1000 tons)	Oil (1000 bbls)	Gas (10^6 cu ft)	Coal (1000 tons)	Oil (1000 bbls)	Gas (10^6 cu ft)	Coal (1000 tons)	Oil (1000 bbls)	Gas (10^6 cu ft)	Coal (1000 tons)	Oil (1000 bbls)	Gas (10^6 cu ft)
Industrial																					
Food and kindred products	0.02	2.50	84.61	0.04	1.11	1.34	8.36	3.63	16.61	2.49	16.17	3.20	0.03	1.10	60.14	2.97	0.07	0.15	1.40	0.15	0.48
Textile mill products	<0.01	0.23	2.34	<0.01	0.15	0.01	0.26	0.26	0.21	1.50	4.92	0.27	—	0.01	1.60	0.06	0.01	<0.01	0.05	<0.01	0.01
Apparel and related products	<0.01	0.01	1.05	—	0.02	0.02	0.38	0.13	0.66	0.40	1.53	0.60	<0.01	<0.01	0.66	0.01	<0.01	0.01	0.02	0.02	0.03
Lumber (exclusive of furniture)	<0.01	0.87	0.66	<0.01	0.92	0.01	0.20	0.10	0.07	0.08	0.44	—	<0.01	0.28	0.35	0.02	<0.01	<0.01	0.12	0.10	<0.01
Furniture and fixtures	<0.01	0.02	0.87	—	0.05	0.01	0.44	0.29	1.18	0.28	0.53	0.24	—	0.01	0.77	0.04	0.01	0.04	0.09	0.01	0.06
Paper and allied products	—	0.62	16.97	—	1.93	0.02	2.08	1.15	4.07	4.08	2.88	0.21	—	0.22	9.45	0.57	0.03	0.01	0.01	<0.01	0.02
Printing and publishing industry	—	0.28	2.35	—	0.01	0.14	0.18	0.68	4.14	0.10	1.04	0.77	—	0.01	1.52	0.02	0.01	0.04	<0.01	0.02	0.20
Chemicals and allied products	0.01	5.53	35.46	—	0.24	0.17	4.40	2.82	16.00	4.93	9.99	0.51	0.01	2.86	21.35	1.05	0.27	0.10	0.46	0.08	0.29
Petroleum and coal products	—	1.70	292.00	—	0.08	0.06	1.58	1.50	97.63	0.38	1.21	0.63	—	0.51	143.06	0.11	0.05	2.99	0.09	0.15	1.88
Rubber products	—	0.50	6.08	—	0.01	—	0.12	0.14	0.19	0.26	0.29	0.04	—	0.25	4.93	0.60	0.01	0.01	—	—	—
Leather and leather products	—	—	—	—	—	—	0.31	0.08	0.08	0.40	0.63	0.06	—	0.02	0.24	0.02	<0.01	<0.01	0.04	—	0.03
Stone, clay, and glass products	0.02	10.34	92.80	0.02	0.92	0.02	3.30	3.70	58.86	2.48	13.37	2.07	0.02	3.66	53.30	1.21	0.16	1.34	0.42	0.05	3.29
Primary metal industries	0.67	3.90	96.58	0.10	0.58	0.18	19.22	25.20	967.78	10.82	39.52	147.20	0.50	1.17	47.05	5.92	3.87	26.78	1.72	1.37	4.13
Fabricated metal products	0.02	0.12	8.30	<0.01	0.06	0.44	0.93	2.73	19.72	0.41	4.84	1.79	0.02	0.05	5.90	0.19	0.14	0.27	0.10	0.03	1.25
Machinery (exclusive of electrical)	0.01	0.21	6.62	<0.01	0.12	0.18	2.82	3.15	22.02	1.05	2.91	1.44	0.01	0.06	3.23	0.31	0.15	0.48	0.08	0.17	0.52
Electrical machinery	<0.01	0.14	6.67	—	0.02	0.28	0.95	1.10	4.75	0.91	2.84	1.25	<0.01	0.02	1.40	0.09	0.10	0.11	<0.01	0.01	0.15
Transportation equipment	<0.01	0.60	14.37	—	0.05	0.08	0.53	0.89	2.36	0.63	5.07	1.26	<0.01	0.13	6.22	0.15	0.06	0.13	—	—	—
Instruments, related products	0.01	<0.01	0.65	—	—	—	0.16	0.35	1.02	0.68	0.61	1.26	—	<0.01	0.24	0.01	<0.01	0.01	—	—	—
Miscellaneous manufacturers	<0.01	0.09	1.98	—	0.01	0.05	0.26	0.60	1.48	0.46	1.26	0.63	<0.01	0.01	0.57	0.06	0.03	0.03	0.16	0.03	0.04
TOTAL	0.76	27.70	673.72	0.18	6.27	2.99	46.48	48.47	1218.83	32.33	110.06	163.42	0.99	10.38	361.46	10.74	4.98	32.48	4.76	2.17	12.36
Railroads, vessels, military		6.25			3.02			0.19			1.37			7.67			1.08			1.20	
Power plants		28.63			8.34			0.46			35.10			11.53			0.04			0.02	
Public																					
Home use	—	1.97	410.0	—	10.21	17.00	35.52	35.92	144.00	22.47	151.95	287.00	—	2.60	189.00	4.00	2.32	136.00	1.30	1.47	80.00
Car use		6110.00(a)			603.80(a)			4110.00(a)			7080.00(a)			2070.00(a)			678.00(a)			548.00(a)	
Truck use		8.45(b)			1.77(b)			1.46(b)			3.18(b)			2.82(b)			0.31(b)			0.47(b)	

(a) Gasoline, 1000 gal
(b) Diesel oil, 1000 bbl

Table B-II

ENERGY CONSUMPTION BY INDUSTRIAL USERS IN VARIOUS CITIES, 1954*

Classification	10^9 Btu's Consumed Daily						
	Los Angeles	Portland	New York	Chicago	San Francisco	Cincinnati	Louisville
Food, kindred products	135.6	8.4	159.6	245.5	92.0	7.1	35.1
Textile mill products	4.7	1.0	65.4	8.0	2.3	1.4	1.3
Apparel, related products	1.5	0.1	19.4	10.8	0.9	0.2	0.5
Lumber (excluding furniture)	6.2	5.6	4.5	5.4	2.2	0.4	3.5
Furniture, fixtures	1.4	0.3	10.0	14.1	1.1	1.0	2.1
Paper, allied products	27.6	11.4	115.2	62.5	15.3	13.8	0.2
Printing, publishing	5.0	0.1	9.7	14.1	2.1	0.6	0.5
Chemicals, allied products	82.6	1.5	177.8	144.8	47.2	26.7	11.9
Petroleum, coal products	421.8	0.5	17.2	184.5	204.7	6.9	5.8
Rubber products	11.6	0.1	7.9	3.9	8.5	14.5	--
Leather, leather products	--	--	13.3	7.9	0.3	0.6	0.9
Stone, clay, glass products	191.9	6.0	141.3	184.0	97.1	31.9	14.9
Primary metal	175.1	5.9	700.5	1975.0	85.3	202.7	55.2
Fabricated metal	12.8	0.7	40.8	66.2	9.1	4.5	4.5
Machinery (excluding electrical)	10.7	0.9	44.8	117.4	4.9	7.4	3.6
Electrical machinery	10.3	0.3	40.5	36.0	2.0	2.2	0.2
Transportation equipment	28.6	0.4	46.8	21.2	9.6	3.6	--
Instruments	1.1	--	21.6	7.3	0.3	0.1	--
Miscellaneous manufacturing	3.4	0.1	19.2	11.9	1.5	7.3	4.4
TOTAL	1131.9	43.1	1655.1	3120.5	586.4	333.0	144.6

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* Underlined values indicate those industrial classifications which were evaluated for actual emission of air pollutants for each city.

Table B-III

COMPARISON OF POPULATION AND AREA OF CITIES

	Population	Square Miles		Square Miles ($x10^{-6}$) per Capita	
	Standard Metropolitan Area	Standard Metropolitan Area	Industrialized Area	Standard Metropolitan Area	Industrialized Area
Los Angeles	5,000,000	4853	700	970	140
Portland	775,000	3663	300	4720	387
New York	12,000,000	3939	500	328	42
Chicago	6,000,000	3617	700	603	117
San Francisco	2,250,000	3314	500	1470	222
Cincinnati	904,000	730	400	808	442
Louisville	577,000	908	200	1570	346

Table B-IV

EMISSIONS FROM MUNICIPAL INCINERATORS

Component	Tons Emitted/100 Tons Waste Burned	Daily Exhaust Products, Tons	
		New York(a)	Chicago(b)
Aldehydes,as HCHO	0.055	2.75	1.38
Ammonia	0.015	0.75	0.38
Nitrogen oxides,as NO_2	0.105	5.25	2.63
Acids,as CH_3COOH	0.030	1.50	0.75
Organics	0.070	3.50	1.75
Solids	1.150	57.50	28.80
Sulfur oxides,as SO_2	0.095	4.75	2.38

(a) 5000 tons/day refuse burned
(b) 2500 tons/day refuse burned

Table B-V

EMISSIONS FROM COMMERCIAL INCINERATORS

Component	Tons Emitted/100 Tons Waste Burned	Daily Exhaust Products, Tons	
		New York(a)	Chicago(b)
Aldehydes,as HCHO	0.055	1.65	0.83
Ammonia	0.015	0.45	0.23
Nitrogen oxides,as NO_2	0.105	3.15	1.58
Acids, as CH_3COOH	0.030	0.90	0.45
Organics	0.070	2.10	1.05
Solids	1.150	34.50	17.30
Sulfur oxides,as SO_2	0.095	2.85	1.43

(a) 3000 tons/day refuse burned
(b) 1500 tons/day refuse burned

Table B-VI

EMISSIONS FROM BACKYARD INCINERATORS

Component	Tons Emitted/100 Tons Waste Burned	Daily Exhaust Products, Tons	
		New York(a)	Chicago(b)
Aldehydes,as HCHO	0.200	3.60	1.80
Ammonia	0.115	2.07	1.04
Nitrogen oxides,as NO_2	0.030	0.54	0.27
Acids, as CH_3COOH	0.075	1.35	0.68
Organics	14.000	252.00	126.00
Solids	1.120	20.2	10.1
Sulfur oxides,as SO_2	0.060	1.08	0.54

(a) 1800 tons/day refuse burned
(b) 900 tons/day refuse burned

Table B-VII

EXHAUST EMISSIONS FROM PUBLIC CONSUMPTION OF FUEL OIL

Component	Tons Emitted/Ton Fuel Oil Burned	Daily Exhaust Products, Tons	
		New York(a)	Chicago(b)
Sulfur dioxide	0.020	498.0	117.70
Sulfur trioxide	0.001	24.9	5.88
Hydrogen sulfide	<0.001	< 24.9	< 5.88
Nitrogen oxide, as NO_2	0.007	174.0	41.20
Hydrogen cyanide	<0.001	< 24.9	< 5.88
Ammonia	0.001	24.9	5.88
Hydrogen chloride	<0.001	< 24.9	< 5.88
Formaldehyde	0.001	24.9	5.88
Organics	0.005	124.5	29.40
Acids, as CH_3COOH	0.015	374.0	88.40
Solids	0.001	24.9	5.88

(a) 151,950 bbl/day (24,900 tons) consumed
(b) 35,917 bbl/day (5,880 tons) consumed

Table B-VIII

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EXHAUST EMISSIONS FROM PUBLIC CONSUMPTION OF MANUFACTURED OR NATURAL GAS

Component	Tons Emitted/Million Cu Ft Gas Burned	Daily Exhaust Products, Tons	
		New York(a)	Chicago(b)
Sulfur dioxide	0.014 28	4.02	2.01
Sulfur trioxide	0.001 2	0.29	0.15
Hydrogen sulfide	0.003 6	0.86	0.43
Nitrogen oxide, as NO_2	0.240 480	68.9	34.50
Hydrogen cyanide	--	--	--
Ammonia	0.010 20	2.87	1.44
Hydrogen chloride	0.010 20	2.87	1.44
Formaldehyde	0.030 60	8.61	4.31
Organics	0.050 100	14.4	7.20
Acids, as CH_3COOH	0.045 90	12.9	6.50
Solids	0.003 6	0.86	0.43

(a) 287×10^6 cu ft/day burned
(b) 144×10^6 cu ft/day burned

Table B-IX

EXHAUST EMISSIONS FROM PUBLIC CONSUMPTION OF COAL

Component	Tons Emitted/Ton Coal Burned	Daily Exhaust Products, Tons	
		New York(a)	Chicago(b)
Sulfur dioxide	0.020	449.4	710.3
Sulfur trioxide	0.001	22.5	35.5
Hydrogen sulfide	<0.001	<22.5	<35.5
Nitrogen oxide, as NO_2	0.004	89.9	142.1
Hydrogen cyanide	<0.001	<22.5	<35.5
Ammonia	0.001	22.5	35.5
Hydrogen chloride	0.001	22.5	35.5
Formaldehyde	0.001	22.5	35.5
Organics	0.010	224.7	355.2
Acids, as CH_3COOH	0.015	337.1	532.7
Solids	0.100	2247.1	3551.6
Fluorides, as F	0.0002	4.4	7.1

(a) 22,471 tons/day burned

(b) 35,516 tons/day burned

Table B-X

ESTIMATED LOSSES FROM AUTOMOBILE EXHAUST

Component	Tons Lost/100,000 gal Gasoline Burned	Daily Exhaust Products, Tons	
		New York(a)	Chicago(b)
Total hydrocarbon, as C_6H_{14}	31.61	2240.0	1300.0
C_3+ hydrocarbon, as C_6H_{14}	9.49	672.0	390.0
Aldehydes, as HCHO	0.17	12.1	6.9
Nitrogen oxide, as NO_2	10.60	750.0	446.0
Sulfur dioxide, as SO_2	1.30	92.0	53.4
Particulate matter	0.45	31.9	18.5
Acids, as CH_3COOH	0.66	46.7	27.1

(a) 168,650 bbl/day (7,080,000 gallons) consumed
(b) 97,875 bbl/day (4,110,000 gallons) consumed

Table B-XI

ESTIMATED HYDROCARBON LOSSES FROM GASOLINE HANDLING OPERATIONS

Operation	Tons Lost in Handling/ 100,000 gal Gasoline	Daily Handling Losses, Tons	
		New York(a)	Chicago(b)
Marketing	0.76	53.8	31.2
Filling service station tanks	0.49	35.7	20.1
Filling auto tanks	0.58	41.0	23.8
Evaporation from auto tanks and carburetors	3.37	239.0	138.4
TOTAL		369.5	213.5

(a) 7,080,000 gal/day burned
(b) 4,110,000 gal/day burned

Table B-XII

ESTIMATED LOSSES FROM DIESEL EXHAUST

Component	Tons Lost/1000 bbl Diesel Oil Burned	Daily Exhaust Products, Tons	
		New York(a)	Chicago(b)
Total hydrocarbons, as C_6H_{14}	3.86	12.3	5.65
C_3+ hydrocarbons, as C_6H_{14}	3.00	9.55	4.39
Aldehydes, as HCHO	0.21	0.67	0.31
Nitrogen oxide, as NO_2	2.19	6.97	3.20
Sulfur dioxide, as SO_2	0.93	2.96	1.36
Particulate matter	2.33	7.42	3.41
Acids, as CH_3COOH	0.83	2.64	1.22

(a) 3182 bbl/day consumed
(b) 1463 bbl/day consumed

600 and 500 tons for all of the other categories listed in Tables B-IV to B-XII. The evolution of oxides of nitrogen from automobile exhaust was double that from the other sources mentioned above. The emission of solids from the public consumption of coal amounted to 2200 and 3500 tons daily for New York and Chicago, and the solids emission from all other sources tabulated in Tables B-IV to B-XII amounted to 150 and 80 tons respectively.

From such data it is possible to determine where the greatest weight of definite air pollutants within specified areas are evolved.

III Emissions from Industrial Activities

Tables B-XIII to B-XXVI give examples of the type of calculations used to determine the potential air pollutant emissions from industrial sources.

Industry was divided into the 20 standard classifications of the Census of Manufacturers. It was assumed that industries which consume the greatest weight of fuels (solid, liquid, and gaseous) are those emitting the largest amount of air pollutants to the atmosphere. As stack emissions are associated with combustion or combustion processes, the heat value of the fuels in British thermal units was used as a criterion of emissions. If a number of such industries consume the largest percentage of fuel values and if it is possible to evaluate the total stack losses from these industrial classifications, then the total emissions from all industrial sources can be calculated on a Btu basis.

Such an approach is naturally open to numerous questions. Objections to the approach of calculating the industrial emissions by the present method were carefully considered, and it is believed that the method offers a justifiable first approximation of the potential weight emission of air pollutants from industrial sources.

Table B-II listed the industrial classifications which were actually evaluated for the emitted air pollutants. Tables B-XVII to B-XXVI give the detailed method of calculations.

The emissions from the primary metals industry are used as a specific example. The following types of operations are included under the classification of primary metal industries, according to the Census of Manufacturers:

Blast furnaces and steel mills
Iron and steel foundries
Primary nonferrous foundries
Secondary nonferrous metals
Nonferrous metal rolling and drawing
Nonferrous foundries
Miscellaneous primary metal industries

Table B-XIII

EXHAUST EMISSIONS FROM POWER PLANTS USING FUEL OIL

Component	Tons Emitted/Ton Fuel Oil Burned	Daily Exhaust Products, Tons	
		New York(a)	Chicago(b)
Sulfur dioxide	0.020	115.2	1.50
Sulfur trioxide	0.001	5.76	0.07
Hydrogen sulfide	<0.001	< 5.76	<0.07
Nitrogen oxide,as NO_2	0.007	40.3	0.52
Hydrogen cyanide	<0.001	<5.76	<0.07
Ammonia	0.001	5.76	0.07
Hydrogen chloride	<0.001	<5.76	<0.07
Formaldehyde	0.001	5.76	0.07
Organics	0.005	28.8	0.37
Acids,as CH_3COOH	0.015	86.5	1.12
Solids	0.001	5.76	0.07

(a) 35,098 bbl/day (5760 tons) consumed

(b) 456 bbl/day (74.8 tons) consumed

Table B-XIV

EXHAUST EMISSIONS FROM FUEL OIL CONSUMPTION BY MILITARY, RAILROADS, VESSELS

Component	Tons Emitted/Ton Fuel Oil Burned	Daily Exhaust Products, Tons	
		New York(a)	Chicago(b)
Sulfur dioxide	0.020	27.4	3.71
Sulfur trioxide	0.001	1.37	0.19
Hydrogen sulfide	<0.001	<1.37	<0.19
Nitrogen oxide,as NO_2	0.007	9.60	1.30
Hydrogen cyanide	<0.001	<1.37	<0.19
Ammonia	0.001	1.37	0.19
Hydrogen chloride	<0.001	<1.37	<0.19
Formaldehyde	0.001	1.37	0.19
Organics	0.005	6.85	0.93
Acids,as CH_3COOH	0.015	20.6	2.78
Solids	0.001	1.37	0.19

(a) 83,500 bbl/day purchased. Assumed 10% used in area or 8350 bbl/day (1370 tons).

(b) 11,300 bbl/day purchased. Assumed 10% used in area or 1130 bbl/day (185 tons).

Table B-XV

POTENTIAL DAILY EMISSIONS FROM INDUSTRIAL SOURCES IN NEW YORK AREA

Component	Tons Emissions Based upon 5 Categories Evaluated(a)	Total Emissions Based upon Total Btu's Consumed(b)
Sulfur dioxide	760	973
Sulfur trioxide	56	72
Hydrogen sulfide	<61	<78
Nitrogen oxide,as NO_2	209	268
Hydrogen cyanide	<32	<41
Ammonia	42	54
Hydrochloric acid	<48	<61
Formaldehyde	37	47
Organics	386	494
Acids, as CH_3COOH	514	658
Fluorides, as F	3	4
Solids	8017	10,262

(a) 1294×10^9 Btu consumed

(b) 1655×10^9 Btu consumed

Table B-XVI

POTENTIAL DAILY EMISSIONS FROM INDUSTRIAL SOURCES IN CHICAGO AREA

Component	Tons Emissions Based upon 5 Categories Evaluated(a)	Total Emissions Based upon Total Btu's Consumed(b)
Sulfur dioxide	2020	2303
Sulfur trioxide	123	140
Hydrogen sulfide	<135	<154
Nitrogen oxide,as NO_2	404	461
Hydrogen cyanide	<135	<154
Ammonia	84	96
Hydrochloric acid	<86	<98
Formaldehyde	79	90
Organics	1353	1542
Acids,as CH_3COOH	939	1070
Fluorides, as F	8	9
Solids	19,833	22,610

(a) 2733.9×10^9 Btu consumed

(b) 3120.5×10^9 Btu consumed

Table B-XVII

EXHAUST EMISSIONS FROM PRIMARY METAL INDUSTRY

Component	Daily Exhaust Products, Tons	
	New York	Chicago
Sulfur dioxide	246.8	692.8
Sulfur trioxide	12.3	34.6
Hydrogen sulfide	12.3	34.6
Nitrogen oxides, as NO_2	64.3	180.9
Hydrogen cyanide	12.3	34.6
Ammonia	12.3	34.6
Hydrogen chloride	12.3	34.6
Formaldehyde	12.3	34.6
Organics	12.3	34.6
Acids, as CH_3COOH	98.4	275.9
Fluorides, as F	183.6	515.1
Solids	1.6	4.5
	6171.0	17,320.0

Table B-XVIII

EXHAUST EMISSIONS FROM NONFERROUS FOUNDRIES (PRIMARY METAL INDUSTRY)

Component	Tons Emitted/Plant Producing 50 tons/day Castings	Daily Exhaust Products, Tons	
		New York(a)	Chicago(b)
Sulfur dioxide	0.040	100.1	282.0
Sulfur trioxide	0.002	5.0	14.1
Hydrogen sulfide	0.002	5.0	14.1
Nitrogen oxide, as NO_2	0.014	35.0	98.7
Hydrogen cyanide	0.002	5.0	14.1
Ammonia	0.002	5.0	14.1
Hydrogen chloride	0.002	5.0	14.1
Formaldehyde	0.002	5.0	14.1
Organics	0.010	25.0	70.5
Acids, as CH_3COOH	0.030	75.1	211.5
Solids	1.0	2502.0	7050.0

50 tons/day casting requires 70 x 10^6 Btu/day

(a) 350.3 x 10^9 Btu/day. Emissions reduced by 50% because of control measures installed

(b) 987.5 x 10^9 Btu/day. Emission reduced by 50%

Table B-XIX

EXHAUST EMISSIONS FROM GRAY IRON FOUNDRIES (PRIMARY METALS INDUSTRY)

Components	Tons Emitted/Plant Producing 200 ton/day Castings	Daily Exhaust Products, Tons	
		New York(a)	Chicago(b)
Sulfur dioxide	0.46	146.7	410.8
Sulfur trioxide	0.023	7.3	20.5
Hydrogen sulfide	0.023	7.3	20.5
Nitrogen oxide,as NO_2	0.092	29.3	82.2
Hydrogen cyanide	0.023	7.3	20.5
Ammonia	0.023	7.3	20.5
Hydrogen chloride	0.023	7.3	20.5
Formaldehyde	0.023	7.3	20.5
Organics	0.23	73.4	205.4
Acids,as CH_3COOH	0.34	108.5	303.6
Solids	11.5	3669.0	10,270.0
Fluorides, as F	0.005	1.6	4.5

200 tons/day requires 0.55 x 10^9 Btu's

(a) 350.3 x 10^9 Btu/day. Emissions reduced by 50% because of control measures installed.

(b) 987.5 x 10^9 Btu/day. Emissions reduced by 50%

Table B-XX

EXHAUST EMISSIONS FROM FOOD AND KINDRED PRODUCTS INDUSTRY

Component	Daily Exhaust Products, Tons	
	New York	Chicago
Sulfur dioxide	206.5	358.3
Sulfur trioxide	10.3	17.9
Hydrogen sulfide	<10.3	<18.0
Nitrogen oxides,as NO_2	58.6	83.2
Hydrogen cyanide	<10.3	<17.9
Ammonia	10.4	18.2
Hydrogen chloride	<10.4	<18.2
Formaldehyde	10.6	18.9
Organics	75.0	174.9
Acids, as CH_3COOH	154.6	270.2
Fluorides, as F	1.0	3.3
Solids	502.9	1673.0

Table B-XXI

EXHAUST PRODUCTS FROM FOOD AND KINDRED PRODUCTS INDUSTRY

Component	Daily Exhaust Products, tons					
	New York(a)			Chicago(b)		
	Coal	Oil	Gas	Coal	Oil	Gas
Sulfur dioxide	99.6	106.0	0.1	334.4	23.4	0.5
Sulfur trioxide	5.0	5.3	--	16.7	1.19	--
Hydrogen sulfide	<5.0	<5.3	--	<16.7	<1.2	0.1
Nitrogen oxide,as NO_2	20.0	37.1	1.5	66.9	8.3	8.0
Hydrogen cyanide	<5.0	<5.3	--	<16.7	<1.2	--
Ammonia	5.0	5.3	0.1	16.7	1.2	0.3
Hydrogen chloride	5.0	<5.3	0.1	16.7	<1.2	0.3
Formaldehyde	5.0	5.3	0.3	16.7	1.2	1.0
Organics	48.0	26.5	0.5	167.2	6.0	1.7
Acids,as CH_3COOH	74.6	79.5	0.5	250.8	17.9	1.5
Solids	497.6	5.3	--	1672.0	1.2	0.1
Fluorides, as F	1.0	--	--	3.3	--	--

(a) 2488 tons coal/day, 16,167 bbl oil/day (2650 tons), 3198x10^3 cu ft/day
Emissions doubled to account for unknown sources
(b) 8361 tons coal/day, 3632 bbl oil/day (596 tons), 16,609x10^3 cu ft/day
Emissions doubled to account for unknown sources

Table B-XXII

EXHAUST EMISSIONS FROM CHEMICAL AND ALLIED PRODUCTS INDUSTRY

Component	Tons Emitted/Chemical Plant Consuming 10^9 Btu/day	Daily Exhaust Products, tons	
		New York(a)	Chicago(b)
Sulfur dioxide	0.914	162.5	132.3
Sulfur trioxide	0.147	26.1	21.3
Hydrogen sulfide	0.024	4.3	3.5
Nitrogen oxide,as NO_2	0.200	35.6	29.0
Hydrogen cyanide	0.022	3.9	3.2
Ammonia	0.078	13.9	11.3
Hydrogen chloride	0.089	15.8	12.9
Formaldehyde	0.046	8.2	6.7
Organics	0.993	176.6	143.8
Acids, as CH_3COOH	0.518	92.1	75.0
Solids	1.300	231.1	188.2

(a) 177.8 x 10^9 Btu/day consumed
(b) 144.8 x 10^9 Btu/day consumed

Table B-XXIII

EXHAUST EMISSIONS FROM PAPER AND ALLIED PRODUCTS INDUSTRIES

Component	Tons Emitted/Operation Using 5.05x10^9 Btu/day	Daily Exhaust Products, Tons
		New York (a)
Sulfur dioxide	5.60	63.8
Sulfur trioxide	0.28	3.2
Hydrogen sulfide	2.64	30.1
Nitrogen oxides, as NO_2	1.96	22.3
Hydrogen cyanide	0.14	1.6
Ammonia	0.14	1.6
Hydrogen chloride	0.50	5.7
Formaldehyde	0.14	1.6
Organics	1.40	16.0
Acids, as CH_3COOH	2.10	23.9
Solids	2.18	24.9

200 tons/day sulfite mill - 40 tons fuel oil) 5.05 x 10^9 Btu
250 tons/day kraft mill - 100 tons fuel oil)
(a) 115.2 x 10^9 Btu - reduced emissions by 50% as no kraft or sulfite in general area

Table B-XXIV

EXHAUST EMISSIONS FROM STONE, CLAY, AND GLASS MANUFACTURE

Component	Tons Emitted/Cement Plant Producing 4830 bbl/day	Daily Exhaust Products, Tons	
		New York(a)	Chicago(b)
Sulfur dioxide	3.36	80.3	104.8
Sulfur trioxide	0.17	4.1	5.3
Hydrogen sulfide	0.17	4.1	5.3
Nitrogen oxides, as NO_2	1.18	28.2	36.8
Hydrogen cyanide	0.17	4.1	5.3
Ammonia	0.17	4.1	5.3
Hydrogen chloride	0.17	4.1	5.3
Formaldehyde	0.17	4.1	5.3
Organics	0.84	20.1	26.2
Acids, as CH_3COOH	2.52	60.2	78.6
Solids	90.97	1087.0	1419.0

Based upon oil as fuel, 5.9 x 10^9 Btu/day. Solids emission reduced by 50% because of control equipment installed.
(a) 141.3 x 10^9 Btu/day consumed
(b) 184.0 x 10^9 Btu/day consumed

Table B-XXV

EXHAUST EMISSIONS FROM PETROLEUM PRODUCTS AND COAL INDUSTRY

Component	Tons Emitted/Petroleum Plant;10,000 bbl/day,7.0x10^9 Btu	Daily Exhaust Products, Tons
		Chicago (a)
Sulfur dioxide	55.5	732.0
Sulfur trioxide	3.3	43.6
Hydrogen sulfide	5.6	73.9
Nitrogen oxide,as NO_2	5.6	73.9
Hydrogen cyanide	5.6	73.9
Ammonia	1.1	14.5
Hydrogen chloride	1.1	14.5
Formaldehyde	1.1	14.5
Organics	55.5	732.0
Solids	5.6	73.9

(a) 184.5 x 10^9 Btu. Emissions reduced by 50% because of control measures installed

Table B-XXVI

EMISSIONS FROM SOURCES NOT ELSEWHERE CLASSIFIED

Type Operation	Hydrocarbon Losses Based upon 10^6 Population,tons	Hydrocarbon Losses to the Atmosphere, tons	
		New York(a)	Chicago(b)
Dip and flow painting	4.0	48	24
Brush painting	24.0	288	144
Paint varnishing industry	2.0	24	12
Solvent manufacturing	0.4	5	3
Degreasing operations	2.0	24	12
Spray drying	14.0	168	84
TOTAL		557	279

(a) 12 x 10^6 population

(b) 6 x 10^6 population

It was assumed that the emissions from these industrial classifications could be represented by the emissions from nonferrous foundries (Table B-XVIII) and the gray iron foundries (Table B-XIX). The raw emission data are based upon the assumption that essentially no additional remedial equipment was installed for the removal of contaminants in the stack gases. This latter assumption was followed for each classification, except for those industries where corrective equipment is commonly utilized in modern operations. Where it was known that industrial emissions were controlled, the calculated discharge was reduced according to the estimated degree of reduction.

Thus in the case of the Primary Metals Industry, half of the energy consumption was used to calculate the emissions from the nonferrous foundries and half was used in the gray iron foundries; the total emissions from the primary metals industry were then summed in Table B-XVII.

The remainder of the industrial emissions were calculated in a similar manner. It is believed that such tables are self-explanatory.

The total industrial emissions, excluding those from power plants, railroads, vessels, etc., are summed in Tables B-XV and Tables B-XVI. In these tables the total emissions in the industrial classifications evaluated are multiplied by the ratio of the total Btu's used by all industrial categories to the Btu's consumed in the categories evaluated.

IV Total Emissions from Centers of Population

The calculated emissions of certain air pollutants from all sources for the seven United States cities are summed in Table B-XXVII. Of interest to the method of calculating total emission of cities are Figures B-1 to B-4, prepared from data presented in Tables B-II and B-XXVII.

Figure B-1 shows the relationship between population of standard metropolitan areas and daily industrial energy consumption. These data indicate a good direct relationship up to a population of 5 million inhabitants. The industrial energy consumption for Chicago is high ($> 3000 \times 10^9$ Btu), whereas that for New York is low (1655×10^9 Btu).

Figures B-2 to B-4 show the relationship of the discharged tons of nitrogen oxides (as NO_2), sulfur dioxide, and organic material against the daily industrial energy consumption. Although additional data are required to fix the exact shape of the curve, the semi-direct relationship is clearly indicated. In Figures B-2 to B-4, the difference between the total emissions curve and the industrial emissions curve indicates the contribution by the general public to the weight of the compound discharged. Thus, the general public contributed more oxides of nitrogen and organics than industrial activities, whereas industry contributed largely to the evolution of sulfur dioxide (and solids).

Table B-XXVII

POTENTIAL EXHAUST EMISSIONS OF POPULATED AREAS

Components	Daily Emissions, tons						
	Los Angeles	Portland	New York	Chicago	San Francisco	Cincinnati	Louisville
Sulfur dioxide	735	129	2170	3197	1147	275	130
Sulfur trioxide	51	6	133	182	70	17	8
Hydrogen sulfide	51	12	133	196	101	13	7
Nitrogen oxides, as NO_2	941	114	1355	1103	441	165	104
Hydrogen cyanide	50	5	96	196	99	12	5
Ammonia	42	7	115	141	38	14	8
Hydrochloric acid	33	6	118	141	35	17	7
Formaldehyde	68	14	131	147	49	18	10
Organics	4154	461	4330	3863	2367	453	302
Acids, as CH_3COOH	367	85	1542	1732	194	132	96
Fluorides, as F	1	1	8	16	1	2	1
Solids*	2375	325	12,693	26,236	1966	3185	1152

* Of the total weight of solids discharged, it is estimated that 70 to 90% by weight would settle out of the air stream within a short distance from the emission source.

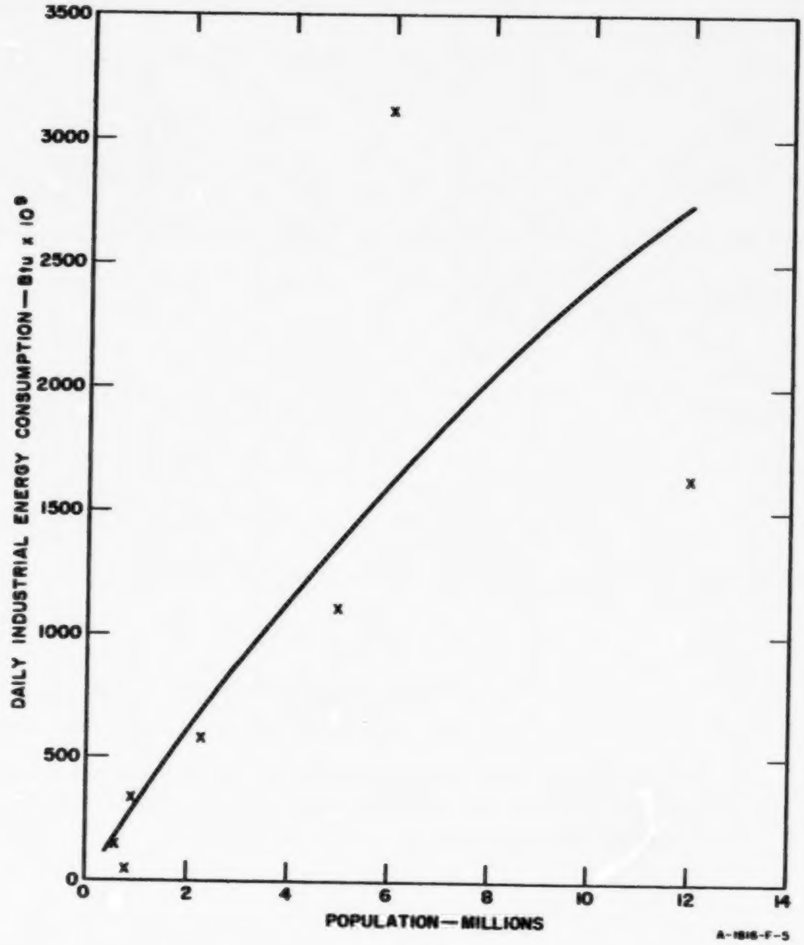

FIG. B-1

INDUSTRIAL ENERGY CONSUMPTION VS POPULATION

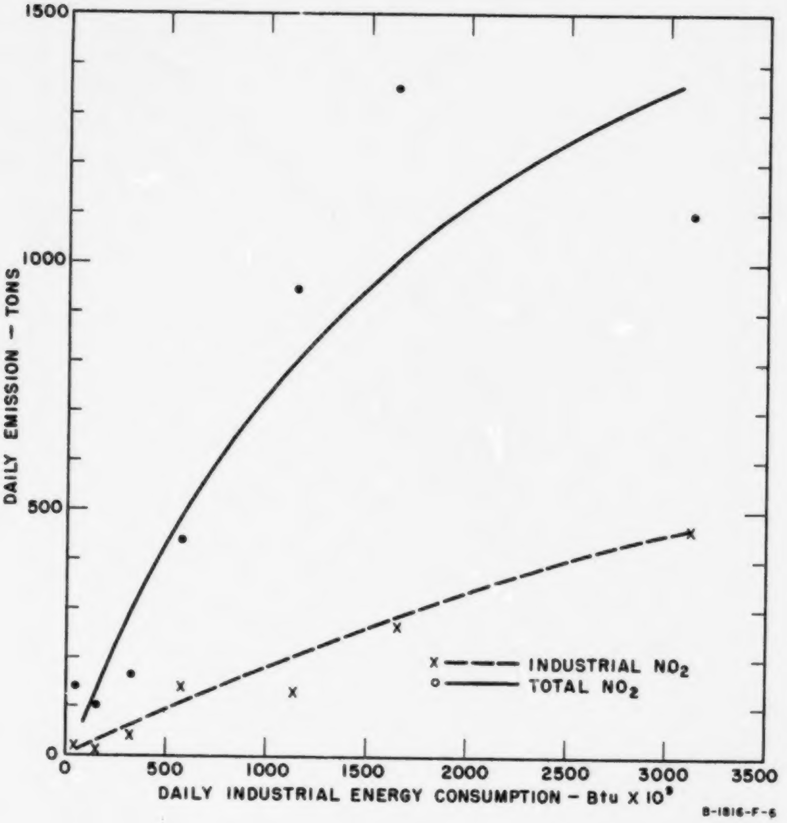

FIG. B-2

EMISSION OF NITROGEN OXIDES AS NO_2 VS ENERGY CONSUMPTION

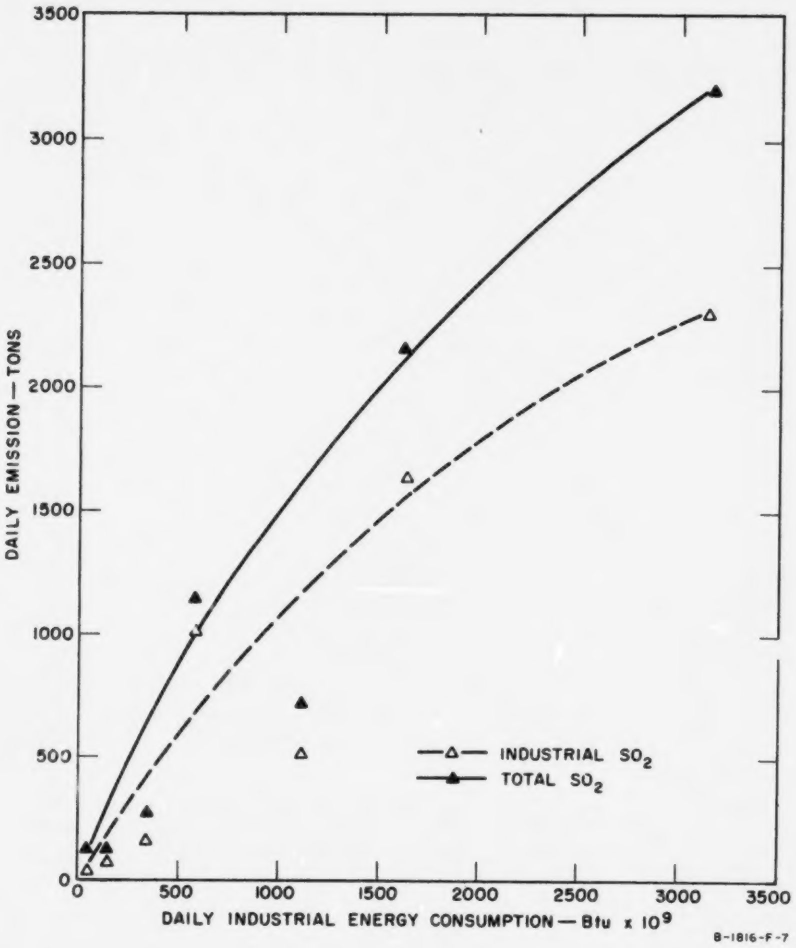

FIG. B-3

EMISSION OF SULFUR DIOXIDE VS ENERGY CONSUMPTION

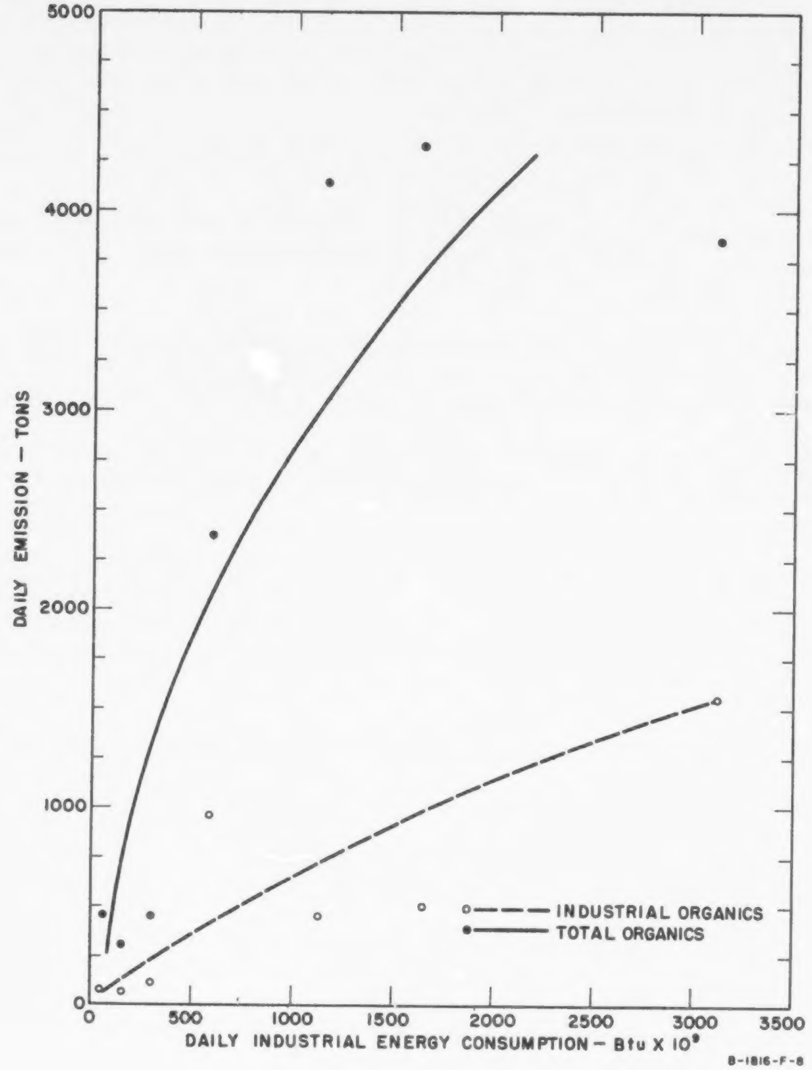

FIG. B-4

EMISSION OF ORGANIC MATERIAL VS ENERGY CONSUMPTION

V Atmospheric Concentration of Air Pollutants

Table B-XXVIII and B-XXIX show the calculated concentrations of certain air pollutants for the standard metropolitan and industrialized areas studied in this report. For these calculations, it was assumed that both the metropolitan area and the industrialized area were square in form. If a definite inversion height and wind speed are postulated, it is possible to estimate the volume of air passing over the area daily. Knowing the total tonnage of a component emitted and the volume of air available for dilution purposes, it is possible to calculate a concentration.

For the calculation, it was also necessary to assume a flat plane and to assume that the effluents were mixed homogeneously in the mass of air throughout the day.

The standard metropolitan and industrial areas are presented in Table B-III. The concentrations for the industrialized area were based upon the entire emissions discharged into this limited area.

The data in Tables B-XXVIII and B-XXIX are valuable in that they show the possible change in concentration for different meteorological conditions.

The "average" concentration of a pollutant was considered to be the concentration calculated for the 1000-ft inversion height for the metropolitan area (Table B-XXVIII). The "average maximum" concentration was considered to be that for a 500-ft inversion for the industrialized area (Table B-XXIX).

VI Prediction of Concentration of Certain Air Pollutants over Cities

An attempt was also made to present the calculated air concentrations in a form which could be used to predict the "average" and "average maximum" concentrations according to population. The results of this research are presented in Figures B-5 to B-8.

Indeed, as mentioned previously, more data are required to confirm the exact relationship between the population of a city and the concentration of air pollutants. The data shown in Figures B-5 to B-8 may be used as a first approximation of the concentration of air pollutants over centers of population.

	Los Angeles			Portland			
	500(a)	1000(b)	2000(c)	500	1000	2000	500
Metropolitan area, sq mi	4853.0	4853.0	4853.0	3663.0	3663.0	3663.0	3939.0
Volume air, cu mi	460.0	919.0	1840.0	346.0	693.0	1390.0	372.0
Volume air, cu mi/day	476.0	1590.0	5080.0	412.0	1370.0	4420.0	428.0
Volume air, 10^{12} cu ft/day	70.0	234.0	747.0	61.0	202.0	650.0	63.0
Weight air, 10^7 tons/day	283.0	945.0	3020.0	244.0	817.0	2620.0	254.0
Volume air, 10^{12} cu m/day	1.98	6.63	21.2	1.71	5.72	18.4	1.7
Calculated Concentrations							
Sulfur dioxide, ppm by vol	0.12	0.04	0.01	0.02	0.01	< 0.01	0.3
Hydrogen sulfide, ppm by vol	0.015	0.004	0.001	0.004	0.001	< 0.001	0.0
Nitrogen oxides (as NO_2), ppm by vol	0.21	0.06	0.02	0.03	0.01	0.003	0.3
Hydrogen cyanide, ppm by vol	0.02	0.005	0.002	0.002	0.001	< 0.001	0.0
Ammonia, ppm by vol	0.03	0.008	0.002	0.005	0.002	< 0.001	0.0
Hydrochloric acid, ppm by vol	0.009	0.003	0.001	0.002	0.001	< 0.001	0.0
Formaldehyde, ppm by vol	0.02	0.007	0.002	0.006	0.002	0.001	0.0
Organics, ppm by vol	0.50	0.15	0.05	0.06	0.02	0.006	0.5
Acids (as acetic acid), ppm by vol	0.06	0.02	0.006	0.02	0.005	0.002	0.2
Fluorides, ppb by wt	0.35	0.16	0.05	0.63	0.19	0.06	3.1
Solids, micrograms/cu m	1090.0	325.0	102.0	172.0	52.0	16.0	6400.0
Solids, tons/sq mi/month	14.7	14.7	14.7	2.7	2.7	2.7	97.0

(a) 3 mph wind
(b) 5 mph wind
(c) 8 mph wind

CALCULATED AIR CONCENTR

Inversion Height - Feet												
Portland			New York			Chicago			San Francisco			
500	1000	2000	500	1000	2000	500	1000	2000	500	1000	2000	50
3663.0	3663.0	3663.0	3939.0	3939.0	3939.0	3617.0	3617.0	3617.0	3314.0	3314.0	3314.0	730
346.0	693.0	1390.0	372.0	745.0	1490.0	342.0	685.0	1370.0	313.0	626.0	1250.0	69
412.0	1370.0	4420.0	428.0	1430.0	4660.0	410.0	1370.0	4390.0	392.0	1308.0	4170.0	184
61.0	202.0	650.0	63.0	210.0	686.0	60.0	202.0	647.0	58.0	192.0	614.0	27
244.0	817.0	2620.0	254.0	850.0	2780.0	242.0	815.0	2620.0	234.0	775.0	2480.0	109
1.71	5.72	18.4	1.79	5.96	19.5	1.71	5.74	18.4	1.65	5.45	17.2	0
0.02	0.01	< 0.01	0.39	0.12	0.04	0.60	0.18	0.06	0.22	0.07	0.02	0
0.004	0.001	< 0.001	0.05	0.013	0.004	0.07	0.02	0.006	0.04	0.011	0.003	0
0.03	0.01	0.003	0.34	0.10	0.03	0.29	0.09	0.03	0.12	0.04	0.01	0
0.002	0.001	< 0.001	0.04	0.012	0.004	0.08	0.02	0.008	0.04	0.013	0.004	0
0.005	0.002	< 0.001	0.08	0.02	0.007	0.10	0.03	0.009	0.03	0.008	0.003	0
0.002	0.001	< 0.001	0.04	0.011	0.003	0.05	0.014	0.004	0.012	0.004	0.001	0
0.006	0.002	0.001	0.05	0.015	0.005	0.06	0.017	0.005	0.02	0.007	0.002	0
0.06	0.02	0.006	0.57	0.17	0.05	0.54	0.16	0.05	0.34	0.10	0.03	0
0.02	0.005	0.002	0.29	0.09	0.03	0.35	0.10	0.03	0.04	0.012	0.04	0
0.63	0.19	0.06	3.1	0.94	0.29	6.6	2.0	0.61	0.43	0.13	0.04	1
172.0	52.0	16.0	6400.0	1930.0	590.0	14,000.0	4100.0	1300.0	1100.0	330.0	100.0	3800
2.7	2.7	2.7	97.0	97.0	97.0	220.0	220.0	220.0	18.0	18.0	18.0	130

Table B-XXVIII

CALCULATED AIR CONCENTRATIONS OF CERTAIN COMPONENTS - METROPOLITAN AREA

ht - Feet

Chicago			San Francisco			Cincinnati			Louisville		
500	1000	2000	500	1000	2000	500	1000	2000	500	1000	2000
3617.0	3617.0	3617.0	3314.0	3314.0	3314.0	730.0	730.0	730.0	908.0	908.0	908.0
342.0	685.0	1370.0	313.0	626.0	1250.0	69.0	138.0	276.0	86.0	172.0	344.0
410.0	1370.0	4390.0	392.0	1308.0	4170.0	184.0	614.0	1960.0	206.0	685.0	2200.0
60.0	202.0	647.0	58.0	192.0	614.0	27.0	90.0	288.0	30.0	101.0	324.0
242.0	815.0	2620.0	234.0	775.0	2480.0	109.0	364.0	1160.0	121.0	405.0	1310.0
1.71	5.74	18.4	1.65	5.45	17.2	0.77	2.56	8.18	0.85	2.85	9.20
0.60	0.18	0.06	0.22	0.07	0.02	0.11	0.03	0.01	0.05	0.01	0.005
0.07	0.02	0.006	0.04	0.011	0.003	0.010	0.003	0.001	0.005	0.001	0.001
0.29	0.09	0.03	0.12	0.04	0.01	0.10	0.03	0.009	0.05	0.016	0.005
0.08	0.02	0.008	0.04	0.013	0.004	0.011	0.003	0.001	0.004	0.001	0.001
0.10	0.03	0.009	0.03	0.008	0.003	0.02	0.007	0.002	0.01	0.003	0.001
0.05	0.014	0.004	0.012	0.004	0.001	0.012	0.004	0.001	0.005	0.001	0.001
0.06	0.017	0.005	0.02	0.007	0.002	0.016	0.005	0.002	0.008	0.002	0.001
0.54	0.16	0.05	0.34	0.10	0.03	0.14	0.04	0.013	0.08	0.03	0.008
0.35	0.10	0.03	0.04	0.012	0.04	0.06	0.02	0.006	0.04	0.011	0.004
6.6	2.0	0.61	0.43	0.13	0.04	1.8	0.55	0.17	0.83	0.25	0.08
14,000.0	4100.0	1300.0	1100.0	330.0	100.0	3800.0	1100.0	350.0	1200.0	370.0	110.0
220.0	220.0	220.0	18.0	18.0	18.0	130.0	130.0	130.0	35.0	35.0	35.0

	Los Angeles			Portland			New	
	500(a)	1000(b)	2000(c)	500	1000	2000	500	1000
Metropolitan area, sq mi	700.0	700.0	700.0	300.0	300.0	300.0	500.0	500.
Volume air, cu mi	66.3	132.4	265.0	28.4	56.7	113.6	47.3	94.
Volume air, cu mi/day	180.0	602.0	1930.0	118.0	393.0	1260.0	152.0	506.
Volume air, 10^{12} cu ft/day	26.4	88.5	284.0	17.3	57.8	185.0	22.0	75.
Weight air, 10^7 tons/day	107.0	358.0	1150.0	70.0	233.0	748.0	89.0	303.
Volume air, 10^{12} cu m/day	0.75	2.5	8.05	0.49	1.64	5.24	0.63	2.
Calculated Concentrations								
Sulfur dioxide, ppm by vol	0.33	0.10	0.03	0.09	0.03	0.01	1.1	0.
Hydrogen sulfide, ppm by vol	0.04	0.012	0.004	0.015	0.004	0.001	0.13	0.
Nitrogen oxides (as NO_2), ppm by vol	0.56	0.17	0.05	0.10	0.03	0.01	0.96	0.
Hydrogen cyanide, ppm by vol	0.05	0.01	0.005	0.007	0.002	0.001	0.11	0.
Ammonia, ppm by vol	0.07	0.02	0.006	0.02	0.005	0.002	0.22	0.
Hydrochloric acid, ppm by vol	0.02	0.007	0.002	0.007	0.002	0.001	0.11	0.
Formaldehyde, ppm by vol	0.06	0.02	0.006	0.02	0.006	0.002	0.14	0.
Organics, ppm by vol	1.30	0.39	0.12	0.22	0.07	0.02	1.6	0.
Acids (as acetic acid), ppm by vol	0.17	0.05	0.02	0.06	0.02	0.006	0.84	0.
Fluorides, ppb by wgt	0.93	0.44	0.14	1.40	0.67	0.21	9.00	2.
Solids, Micrograms/cu m	2880.0	863.0	268.0	602.0	180.0	56.0	18,300.0	5400.
Solids, tons/sq mi/month	102.0	102.0	102.0	32.5	32.5	32.5	760.0	760.

(a) 3 mph wind
(b) 5 mph wind
(c) 8 mph wind

CALCULA

Inversion Height - Feet												
Portland			New York			Chicago			San Francisco			
500	1000	2000	500	1000	2000	500	1000	2000	500	1000	2000	500
300.0	300.0	300.0	500.0	500.0	500.0	700.0	700.0	700.0	500.0	500.0	500.0	400.0
28.4	56.7	113.6	47.3	94.5	189.0	66.3	132.4	265.0	47.3	94.5	189.0	37.8
118.0	393.0	1260.0	152.0	506.0	1620.0	180.0	602.0	1930.0	152.0	506.0	1620.0	136.0
17.3	57.8	185.0	22.0	75.0	238.0	26.4	88.5	284.0	22.0	75.0	238.0	20.0
70.0	233.0	748.0	89.0	303.0	960.0	107.0	358.0	1150.0	89.0	303.0	960.0	81.0
0.49	1.64	5.24	0.63	2.13	6.76	0.75	2.50	8.05	0.63	2.13	6.76	0.57
0.09	0.03	0.01	1.1	0.32	0.10	1.4	0.41	0.13	0.58	0.17	0.05	0.15
0.015	0.004	0.001	0.13	0.04	0.01	0.16	0.05	0.01	0.10	0.03	0.009	0.014
0.10	0.03	0.01	0.96	0.28	0.09	0.65	0.19	0.06	0.31	0.09	0.03	0.13
0.007	0.002	0.001	0.11	0.03	0.01	0.19	0.06	0.018	0.12	0.03	0.011	0.015
0.02	0.005	0.002	0.22	0.06	0.02	0.23	0.07	0.02	0.07	0.02	0.007	0.03
0.007	0.002	0.001	0.11	0.03	0.01	0.11	0.03	0.01	0.03	0.009	0.003	0.017
0.02	0.006	0.002	0.14	0.04	0.013	0.13	0.04	0.012	0.06	0.018	0.006	0.02
0.22	0.07	0.02	1.6	0.48	0.15	1.2	0.36	0.11	0.90	0.26	0.08	0.19
0.06	0.02	0.006	0.84	0.25	0.008	0.79	0.24	0.07	0.11	0.03	0.01	0.08
1.40	0.67	0.21	9.00	2.60	0.83	14.9	4.5	1.4	1.1	0.33	0.10	2.5
602.0	180.0	56.0	18,300.0	5400.0	1700.0	31,800.0	9500.0	3000.0	2800.0	840.0	260.0	5100.0
32.5	32.5	32.5	760.0	760.0	760.0	1100.0	1100.0	1100.0	120.0	120.0	120.0	240.0

Table B-XXIX

CALCULATED AIR CONCENTRATIONS OF CERTAIN COMPONENTS IN INDUSTRIALIZED AREAS

Inversion Height - Feet

Chicago			San Francisco			Cincinnati			Louisville		
500	1000	2000	500	1000	2000	500	1000	2000	500	1000	2000
700.0	700.0	700.0	500.0	500.0	500.0	400.0	400.0	400.0	200.0	200.0	200.0
66.3	132.4	265.0	47.3	94.5	189.0	37.8	75.6	152.0	18.9	37.8	75.8
180.0	602.0	1930.0	152.0	506.0	1620.0	136.0	454.0	1460.0	96.5	322.0	1005.0
26.4	88.5	284.0	22.0	75.0	238.0	20.0	67.0	215.0	14.0	47.0	147.0
107.0	358.0	1150.0	89.0	303.0	960.0	81.0	271.0	870.0	57.0	190.0	595.0
0.75	2.50	8.05	0.63	2.13	6.76	0.57	1.90	6.11	0.40	1.34	4.17
1.4	0.41	0.13	0.58	0.17	0.05	0.15	0.05	0.01	0.10	0.03	0.01
0.16	0.05	0.01	0.10	0.03	0.009	0.014	0.004	0.001	0.011	0.003	0.001
0.65	0.19	0.06	0.31	0.09	0.03	0.13	0.04	0.01	0.12	0.03	0.01
0.19	0.06	0.018	0.12	0.03	0.011	0.015	0.005	0.001	0.009	0.003	0.001
0.23	0.07	0.02	0.07	0.02	0.007	0.03	0.009	0.003	0.02	0.007	0.002
0.11	0.03	0.01	0.03	0.009	0.003	0.017	0.005	0.002	0.01	0.003	0.001
0.13	0.04	0.012	0.06	0.018	0.006	0.02	0.006	0.002	0.017	0.005	0.002
1.2	0.36	0.11	0.90	0.26	0.08	0.19	0.06	0.02	0.18	0.05	0.017
0.79	0.24	0.07	0.11	0.03	0.01	0.08	0.02	0.007	0.08	0.02	0.008
14.9	4.5	1.4	1.1	0.33	0.10	2.5	0.74	0.23	1.8	0.52	0.17
31,800.0	9500.0	3000.0	2800.0	840.0	260.0	5100.0	1500.0	470.0	2600.0	780.0	250.0
1100.0	1100.0	1100.0	120.0	120.0	120.0	240.0	240.0	240.0	170.0	170.0	170.0

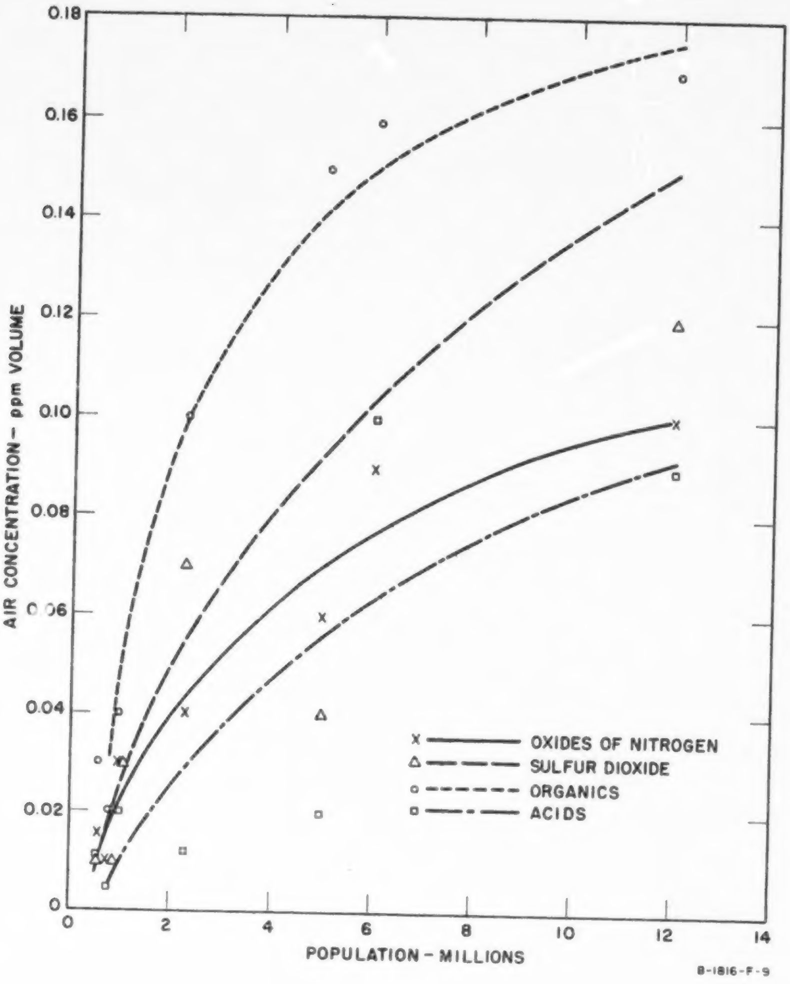

FIG. B-5

CALCULATED AVERAGE CONCENTRATIONS OF AIR POLLUTANTS VS POPULATION

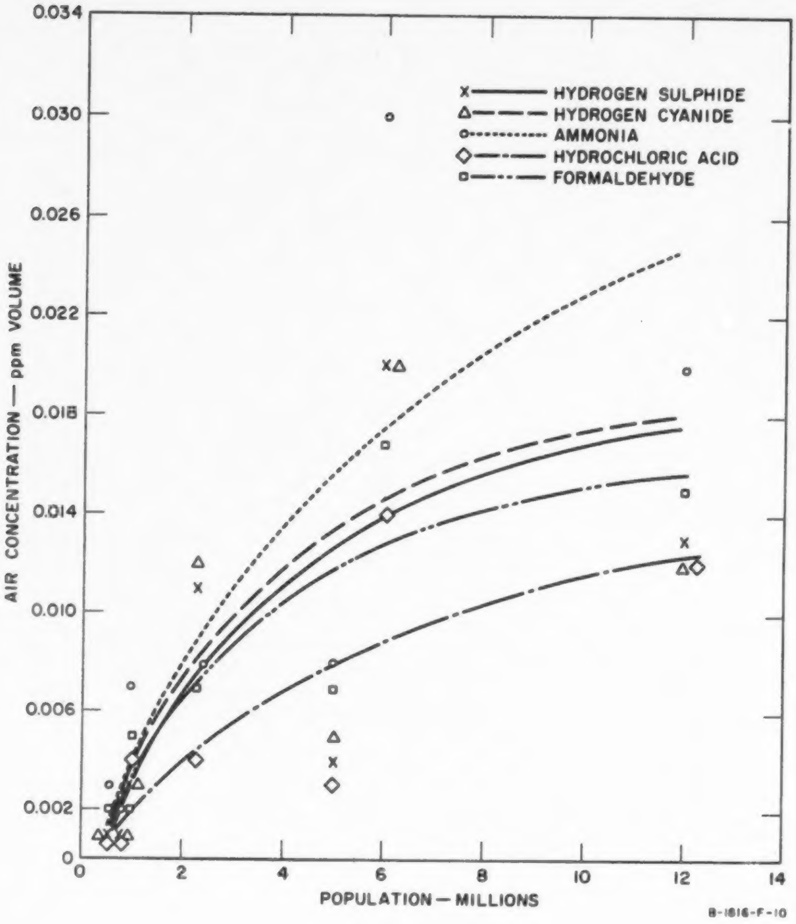

FIG. B-6

CALCULATED AVERAGE CONCENTRATIONS OF AIR POLLUTANTS VS POPULATION

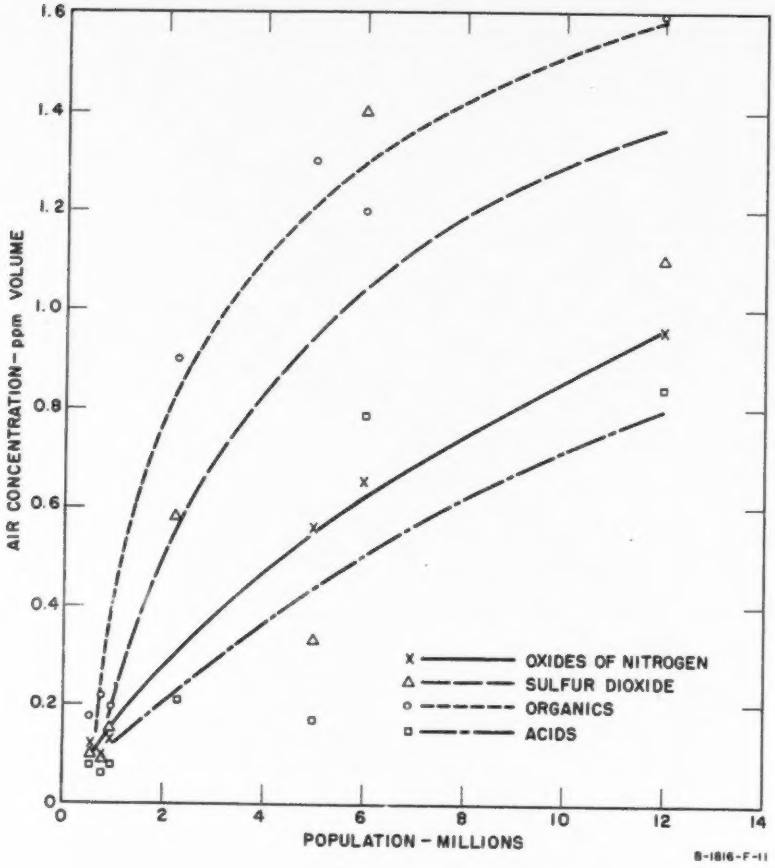

FIG. B-7

CALCULATED AVERAGE MAXIMUM CONCENTRATIONS OF AIR POLLUTANTS VS POPULATION

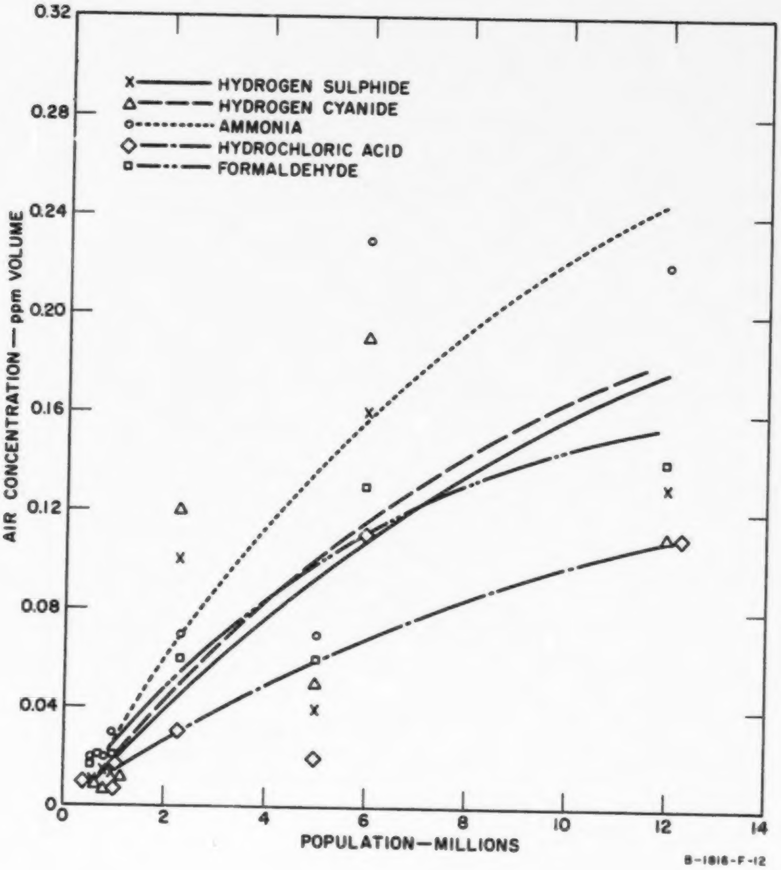

FIG. B-8

CALCULATED AVERAGE MAXIMUM CONCENTRATIONS OF AIR POLLUTANTS VS POPULATION

Appendix C

SUMMARY TABLES OF MEASURED AND CALCULATED AIR POLLUTANTS

I Measured and Calculated Air Concentrations

Table C-I through C-III summarize the literature data on measured air pollutant concentrations throughout the world. The tables were arranged to show the average concentration and concentration range for metropolitan areas of different sizes. These data summarize the results presented in Appendixes A and B, which were obtained from an exhaustive perusal of air pollution literature and document files of Stanford Research Institute.

It will be noted that the average and average maximum concentrations decrease with decreasing population. For the gaseous components sampled most frequently (sulfur dioxide, ozone, and carbon dioxide), the concentration of these components for cities in the population range 500,000 to 2,000,000 was 44 percent that for cities greater than 2,000,000 in population; the concentration in cities of less than 500,000 population was 38 percent that of cities in the largest population group.

The "average" concentration was presented as being indicative of average meteorological conditions. The "average maximum" values were given as representative for polluted atmospheres under adverse meteorological conditions.

The calculated air concentrations for seven metropolitan areas are shown in Tables C-IV and C-V. These data were based upon the calculated emissions of each pollutant from both public and industrial activities and upon assumed meteorological data (Appendix B).

Such calculations were undertaken because the literature data on air concentrations of most pollutants were both meager and incomplete. The mode of calculation made it possible to compare estimated pollutant concentrations with population as well as with the type and extent of industrial activity and fuels consumed.

The cities of Los Angeles and San Francisco burn gas and oil as fuel; Portland burns principally oil. New York, Chicago, Cincinnati, and Louisville are coal-burning cities. Los Angeles and San Francisco produce large quantities of petroleum products, whereas Chicago, New York, Cincinnati, and Louisville produce large quantities of primary metals; Portland is a relatively large producer of paper and paper products.

II Average Air Concentrations Reported by Other Investigators

A few investigators have presented data from which it was possible to prepare tables of average measured air concentrations. These data are presented in Tables C-VI through C-VIII and the results agree very well with similar data shown in Tables C-I through C-V.

Table C-I

VARIATION OF MEASURED AVERAGE GASEOUS AIR POLLUTANT CONCENTRATION WITH SIZE OF METROPOLITAN AREA

(ppm by vol)

	Population Range					
	Greater than 2,000,000		500,000 to 2,000,000		Less than 500,000	
Component	Average Concentration	Concentration Range	Average Concentration	Concentration Range	Average Concentration	Concentration Range
Sulfur dioxide	0.15	0.01-0.48	0.05	0.02-0.09	0.04	0.01-0.17
Hydrogen sulfide	0.10*	--	--	--	0.01*	--
Nitrogen oxide, as NO_2	0.48	0.1-0.9	0.22	0.21-0.23	0.14	0.12-0.15
Ammonia	0.11	0.01-0.22	0.02	--	0.03*	--
Aldehydes, as HCHO	0.24	0.20-0.28*	0.07	0.07	0.04*	--
Hydrocarbons	0.29*	0.2-0.38	--	--	--	--
Chlorine	0.09*	0.08-0.10	0.04	0.03-0.04	0.05*	0.03-0.07
Carbon monoxide	3.4*	2.0-4.8	8.3*	6.5-10.0	5*	--
Ozone	0.07	0.02-0.21	0.03	0.03-0.04	0.03	0.01-0.05
Hydrogen fluoride	0.008*	--	0.006	0.001-0.013	0.005*	0.003-0.007
Carbon dioxide	330*	--	370*	--	--	--

Table C-II

VARIATION OF MEASURED AVERAGE MAXIMUM GASEOUS AIR POLLUTANT CONCENTRATION WITH SIZE OF METROPOLITAN AREA

(ppm by vol)

	Population Range					
	Greater than 2,000,000		500,000 to 2,000,000		Less than 500,000	
Component	Average Concentration	Concentration Range	Average Concentration	Concentration Range	Average Concentration	Concentration Range
Sulfur dioxide	0.72	0.12-1.5	0.36	0.09-0.75	0.21	0.02-0.8
Hydrogen sulfide	0.61*	--	--	--	--	--
Nitrogen oxide, as NO_2	2.05*	0.61-3.5	0.62	0.55-0.67	0.50	0.3-0.63
Ammonia	1.6*	0.2-3.1	0.07	0.05-0.09	0.16*	0.12-0.21
Aldehydes, as HCHO	0.89*	0.85-0.92	0.70*	0.12-1.8	0.37	0.13-0.6
Hydrocarbons	1.10*	0.15-3.0	1.39*	--	--	--
Chlorine	0.38*	0.15-0.62	0.13*	0.11-0.15	0.13	0.03-0.3
Carbon monoxide	109	3-300	19	3-38	1.2*	--
Ozone	0.17	0.05-0.33	0.08	0.08	0.15	0.03-0.33
Hydrogen fluoride	0.027*	--	0.027	0.005-0.05	0.031*	0.030-0.032
Carbon dioxide	980	370-2700	460	400-530	430	--

* Less than 3 cities reported in "average"

Table C-III

VARIATION OF MEASURED PARTICULATE AIR POLLUTANT CONCENTRATION WITH SIZE OF METROPOLITAN AREA

(μg/cu m)

	Population Range					
	Greater than 2,000,000		500,000 to 2,000,000		Less than 500,000	
Component	Average Concentration	Concentration Range	Average Concentration	Concentration Range	Average Concentration	Concentration Range
Aluminum	3.0	0.1-15.3	4.2	0.1	4.5	--
Antimony	<0.2	Tr-0.6	--	--	--	--
Arsenic	0.07	0.0-0.04	0.01	0.0-0.06	0.04	--
Barium	0.04	0.02-0.16	--	--	0.08	--
Beryllium	<0.002	0.00-0.01	0.0014	--	0.0002	--
Bismuth	0.02	0.00-0.04	--	--	--	--
Cadmium	0.005	0.00-0.05	0.13	--	0.001	--
Calcium	2.9	0.85-13.9	16.0	0.4-65.0	1.9	--
Chloride ion	0.80	0.10-3.7	1.9	0.2-6.6	2.5	--
Chromium	0.013	0.00-0.18	--	--	--	--
Cobalt	Tr	0.00-0.012	--	--	--	--
Copper	0.35	0.04-1.02	0.3	0.01-0.5	0.33	--
Fluoride ion	0.31	0.00-6.3	0.19	0.10-2.9	0.13	--
Iron	6.5	0.7-10.8	6.7	0.10	3.9	--
Lead	3.2	0.23-4.5	1.0	0.13-1.8	0.65	--
Magnesium	4.6	0.27-8.5	0.81	0.2-2.6	0.26	--
Manganese	0.95	0.02-0.6	0.19	--	0.19	--
Molybdenum	0.04	Tr-0.09	--	--	0.01	--
Mercury	--	--	0.10	0.03-0.21	0.7	--
Nickel	0.015	0.003-0.22	--	--	0.0	--
Nitrate ion	9.6	--	1.0	--	0.8	--
Potassium	3.6	--	--	--	--	--
Silica	16.4	1.95-49.5	30.5	--	37.5	--
Sulfate ion	12.1	0.1-144.0	1.21	--	4.56	--
Sulfur	--	--	--	--	--	--
Tin	0.05	Tr-0.14	0.03	0.01	0.01	--
Titanium	0.23	0.002-0.89	0.26	0.005-0.89	0.10	--
Tungsten	0.009	0.00-0.30	--	--	--	--
Vanadium	0.05	0.00-0.09	0.05	--	0.01	--
Zinc	0.23	0.00-2.07	2.0	--	1.6	--
Total Particulate	525	230-915	340	104-630	270	55-720
Ash	175	140-200	190	140-200	--	--
Acetone soluble matter	--		21.8	15.8-34.4	18.0	

Table C-IV

"AVERAGE" CALCULATED AIR CONCENTRATIONS FOR CERTAIN METROPOLITAN AREAS
(ppm by vol)

	Metropolitan Areas						
Component	Los Angeles	Portland	New York	Chicago	San Francisco	Cincinnati	Louisville
Sulfur dioxide	0.04	0.01	0.12	0.18	0.07	0.03	0.01
Sulfur trioxide	--	--	--	--	--	--	--
Hydrogen sulfide	0.004	0.001	0.013	0.02	0.011	0.003	0.001
Nitrogen oxide,as NO_2	0.06	0.01	0.10	0.09	0.04	0.03	0.016
Hydrogen cyanide	0.005	0.001	0.012	0.02	0.013	0.003	0.001
Ammonia	0.008	0.002	0.02	0.03	0.008	0.007	0.003
Hydrochloric acid	0.003	0.001	0.011	0.014	0.004	0.004	0.001
Formaldehyde	0.007	0.002	0.015	0.017	0.007	0.005	0.002
Organics	0.15	0.02	0.17	0.16	0.10	0.04	0.03
Acids,as CH_3COOH	0.02	0.005	0.09	0.10	0.012	0.02	0.011
Fluorides,as F*	0.16	0.19	0.94	2.0	0.13	0.55	0.25
Solids**	325	52	1930	4100	330	1100	370

Table C-V

"MAXIMUM" CALCULATED AIR CONCENTRATIONS FOR CERTAIN METROPOLITAN AREAS

	Metropolitan Areas						
Component	Los Angeles	Portland	New York	Chicago	San Francisco	Cincinnati	Louisville
Sulfur dioxide	0.33	0.09	1.1	1.4	0.58	0.15	0.10
Sulfur trioxide	--	--	--	--	--	--	--
Hydrogen sulfide	0.04	0.015	0.13	0.16	0.10	0.014	0.011
Nitrogen oxide,as NO_2	0.56	0.10	0.96	0.65	0.31	0.13	0.12
Hydrogen cyanide	0.05	0.007	0.11	0.19	0.12	0.015	0.009
Ammonia	0.07	0.02	0.22	0.23	0.07	0.03	0.02
Hydrochloric acid	0.02	0.007	0.11	0.11	0.03	0.017	0.01
Formaldehyde	0.06	0.02	0.14	0.13	0.06	0.02	0.017
Organics	1.3	0.22	1.6	1.2	0.90	0.19	0.18
Acids as CH_3COOH	0.17	0.06	0.84	0.79	0.11	0.08	0.08
Fluorides,as F*	0.93	1.4	9.0	14.9	1.1	2.5	1.8
Solids**	2880	602	18,300	31,800	2800	5100	2600

* Parts per billion by weight

** Micrograms per cubic meter

Table C-VI

AVERAGE CONCENTRATIONS OF MATERIALS IN THE AIR

Component	Milligrams/ Cubic Meter	Parts per Million by Volume
Sulfur dioxide	0.07-2.0	0.02-0.07
Nitrogen oxides	0.3-0.5	0.15-0.24
Ammonia	0.01-0.03	0.01-0.04
Aldehydes	0.05-0.1	0.04-0.08
Fluorides, as HF	0.003-0.02	0.003-0.022
Carbon monoxide	5-10	4.0-8.0
Carbon dioxide	600-700	307-358
Sulfate, as SO_4	0.003-0.008	--
Particulate	0.3-0.9	--
Antimony	0.000001-0.000005	
Beryllium	0.000001-0.00001	
Chromium	0.000008-0.00002	
Nickel	0.000006-0.00003	
Molybdenum	0.00001-0.00005	
Cadmium	0.000002- 0.0002	
Tin	0.00001-0.00005	
Vanadium	0.000002-0.0002	
Barium	0.00001-0.00006	
Titanium	0.00005-0.0004	
Manganese	0.0002-0.0003	
Copper	0.00005-0.02	
Magnesium	0.0004-0.0009	
Zinc	0.0003-0.002	
Lead	0.0002-0.003	
Calcium	0.002-0.02	
Iron	0.0008-0.02	
Aluminum	0.003-0.08	
Silicon	0.003-0.008	

Table C-VII

AVERAGE CONCENTRATIONS OF AIR POLLUTANTS MEASURED IN VARIOUS COMMUNITIES

Component	Parts per Million by Volume
Sulfur dioxide	0.15
Nitrogen oxides, as NO_2	0.17
Ammonia	0.02
Aldehydes, as HCHO	0.09
Fluorides, as HF	0.008
Chlorides	0.05
Carbon monoxide	6.8
Carbon dioxide	356.0
Suspended matter (mg/cu m)	0.48

Table C-VIII

AVERAGE CONCENTRATION OF PARTICULATE MATTER -- TAFT SANITARY ENGINEERING CENTER
(μg/cu m)

Component	Maximal Urban Air Loadings	Concentration for Cities of Population over 2,000,000(a)	Concentration for Cities of Population between 500,000 & 2,000,000(b)	Atypical Loadings from Selected Small Cities(c)	Concentration for Non-urban Areas(d)
Total	3112.0	264	136	225	65
Acetone soluble	234.0	44.3	22.8	19.8	9.2
Proteins	110.6	--	--	--	--
Manganese	5.70	0.32	0.16	0.13	0.05
Lead	26.6	4.6	1.7	0.9	0.4
Tin	0.84	0.07	0.02	0.01	<0.01
Iron	53.6	6.5	4.0	6.0	3.3
Copper	4.68	0.49	0.14	0.16	0.10
Silver	0.0746	--			
Titanium	2.57	0.26	0.15	0.33	0.08
Vanadium	0.64	0.105	0.19	0.004	0.002
Chromium	3.5	--	--	--	--
Zinc	0.78	--	--	--	--
Magnesium	15.5	--	--	--	--
Sodium	23.7	--	--	--	--
Potassium	8.7	--	--	--	--
Strontium	1.55	--	--	--	--
Beryllium	0.003	0.0003	0.0002	0.0002	0.0001
Arsenic	1.41	0.06	0.01	0.04	0.02
Fluoride, as F^-	1.64	0.18	0.10	Nil	0.05
Chloride, as Cl^-	7.6	--	--	--	--
Sulfate, as $SO_4^=$	87.8	12.3	2.0	3.6	0.6
Nitrate, as NO_3^-	40.4	3.9	1.2	0.9	0.1
Polycyclic hydrocarbon	29.6	--	--	--	--

(a) Average of 5 cities
(b) Average of 7 cities
(c) Average of 4 cities
(d) Average of 5 cities

III Composition of Synthetic Atmosphere

For the preparation of a synthetic atmosphere to test the viability of bacteria, it is suggested that a high air pollutant concentration be studied first. If test work using "average maximum" concentrations shows no detrimental effects on the candidate bacteria (or a minimum kill) then it might be assumed that there are no bacterio-static or bactericidal substances in atmospheres of cities. If, on the other hand, bactericidal substances are found when the "average maximum" concentrations are used for test purposes, data have also been presented for the "average" air pollutant concentrations of cities.

Such an approach to the over-all problem is not a positive solution to the study. A synthetic atmosphere prepared from approximately 50 different components cannot be expected to be identical with the polluted air over cities where many thousands of different components may be present. The suggested concentrations of air pollutants for the synthetic atmosphere should be considered only as a first approximation of those in the atmosphere of polluted areas.

Tables C-IX and C-X present "average maximum" and "maximum" concentrations of various air pollutants for four different areas. For the preparation of the synthetic atmosphere to be used for bactericidal tests, it is suggested that the concentrations tabulated under the heading, "average maximum concentrations for heavily industrialized areas" be used. This tabulation was based upon both the measured and calculated air pollutant concentrations of populated areas as well as a knowledge of past and present air pollution research. The air pollutant concentrations for Los Angeles, Cincinnati, and Donora are presented for comparison.

An attempt was made to determine if a constant ratio exists between the "maximum" and "average" concentrations of both measured and calculated values. The results of this study are presented in Table C-XI. The over-all average ratio is 4.0, omitting the high values for sulfur dioxide, carbon monoxide, fluoride, and nitrate. Undoubtedly, however, such an average ratio should not be calculated, as too many unknown variables are involved.

IV Constituents of Synthetic Atmosphere

In the preparation of the synthetic atmosphere, attempts have been made to use compounds which are or may be present in polluted atmospheres. Whenever doubt existed as to the actual form of a compound in the atmosphere, the more logical toxic materials was used, namely, the most soluble form.

Presented below are the tentative constituents of the synthetic atmosphere:

Table C-IX

GASEOUS COMPOSITION OF CERTAIN ATMOSPHERES
(ppm by vol)

Component	Average Maximum Concentrations for Heavily Industrialized Areas	High Concentrations Found during Period of Intense Smog in Los Angeles	Highest Concentrations Found	
			Cincinnati, Ohio	Donora, Pa.
Sulfur dioxide	1.0	0.3	0.46	0.50
Sulfur trioxide	0.05	--	0.15	--
Hydrogen sulfide	0.20	--	--	--
Nitrogen oxide, as NO_2	0.9	0.4	0.55	0.63
Ammonia	0.3	--	0.89	--
Aldehydes, as HCHO	0.5	0.4	0.27	--
Hydrocarbons, as C_6H_{14}	1.1	1.1	--	--
Hydrochloric acid	0.2	--	--	0.3
Carbon monoxide	10.0	23.0	55.0	Tr
Carbon dioxide	400.0	--	520.0	--
Ozone	0.2	0.5	0.10	--
Fluorides, as HF	0.008	0.02	0.025	0.06
Organic acids, as CH_3COOH	0.8	0.4	--	--
Hydrogen cyanide	0.1	--		--

Table C-X

PARTICULATE COMPOSITION OF CERTAIN ATMOSPHERES
(μg/cu m)

Component	Average Maximum Concentrations for Heavily Industrialized Areas	Maximum Concentrations Found		
		Los Angeles	Cincinnati	Donora
Total particulate	740.0	1220.0	1980.0	2500.0
Ash	240.0			
Combustible	500.0			
Acetone sol. fraction	30.0	45.0	31.0(avg)	
Silica	20.0			
Fluoride ion	0.3		14.0	
Chloride ion	3.7		6.6	
Nitrate ion	10.0	116.0		
Sulfate ion	144.0	155.0	8.5	
Aluminum	15.3	16.8	25.0	6(avg)
Antimony	0.6			
Arsenic	0.04	0.65		
Barium	0.16	0.24		
Beryllium	0.01	0.002	0.01	
Bismuth	0.04			
Cadmium	0.05		0.42	2(avg)
Calcium	13.9	16.8	65.0	
Chromium	0.18			
Cobalt	0.012			
Copper	1.02	1.4	32.0	1(avg)
Iron	10.8	19.6	110.0	14
Lead	4.5	42.4	11.5	4.5
Magnesium	8.5	19.6	10.0	
Manganese	0.6	1.9	2.0	0.6(avg)
Molybdenum	0.09			
Mercury	0.2		0.21	
Nickel	0.22			
Potassium	10.0	7.2	230.0	
Sulfur	--	49.0		
Tin	0.14	0.96	12.0	<0.2
Titanium	0.89	1.02	20.0	
Tungsten	0.30			
Vanadium	0.09	0.17	0.4	
Zinc	2.07		14.0	40
Silver		0.0027	0.8	0.1(avg)
Sodium		8.6	84.0	
Strontium		1.08		

Table C-XI

RATIO OF "MAXIMUM" TO "AVERAGE" CONCENTRATION OF VARIOUS AIR POLLUTANTS

Component	Calculated Values	Measured Values
Sulfur dioxide	2.3	10.0
Hydrogen sulfide	2.5	5.0
Nitrogen oxide, as NO_2	2.4	8.5
Hydrogen cyanide	2.5	--
Ammonia	3.0	3.2
Hydrochloric acid	1.0	2.2
Formaldehyde	2.5	7.6
Organics	2.4	5.5
Acids, as CH_3COOH	2.3	--
Fluorides, ppb by wt	2.3	4.8
Ozone	--	3.9
Carbon dioxide	--	4.2
Carbon monoxide	--	20.0
Total particulate·	2.3	3.6
Manganese	--	3.3
Lead	--	4.9
Tin	--	8.0
Iron	--	2.2
Vanadium	--	--
Copper	--	3.3
Beryllium	--	5.9
Titanium	--	4.1
Arsenic	--	5.1
Fluorides, as F^-	--	316.0
Sulfate as SO_4^{--}	--	9.8
Nitrate as NO_3^-	--	33.0

Sulfur dioxide	SO_2 gas
Sulfur trioxide	H_2SO_4 aerosol
Hydrogen sulfide	H_2S gas
Oxides of nitrogen	NO_2 gas
Ammonia	NH_3 gas
Aldehydes	60% HCHO
	20% CH_3CHO
	20% Higher aldehydes(acrolein)
Hydrocarbons	25% acetylene
	40% n-hexane
	35% benzene
Carbon monoxide	CO gas
Carbon dioxide	CO_2 gas
Ozone	O_3 gas (plus oxygen)
Fluorides	HF (aspirating solution)
Acids, as CH_3COOH	CH_3COOH
Hydrogen cyanide	HCN gas
Particulate	Water soluble salts where possible -- inject as a water suspension under pressure in sealed ampule

Appendix C

BIBLIOGRAPHY

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3. Chambers, L. A., M. J. Foter, and J. Cholak. A comparison of particulate loadings in the atmospheres of certain American cities. In Proc. Third National Air Pollution Symposium. Stanford Research Institute, Los Angeles, 1955

Appendix D

METHODS FOR INJECTING ATMOSPHERIC POLLUTION SIMULANTS INTO A TEST CHAMBER

I Introduction

The equipment and methods for injection of pollution simulants into a static test chamber have been contrived in accordance with test requirements stipulated by Dr. E. B. Seligmann of Biological Warfare Laboratories, during discussions held on September 25-26, 1956.

For purposes of this discussion, the test chamber is considered to be of 2×10^4 liters capacity and to be operated as a static test facility at a negative pressure of about one inch of water.

The contemplated test program appears directed initially toward testing individual gases and vapors considered to be typical pollutants in the metropolitan atmosphere. Further testing will involve sub-groups of the proposed list of pollutant simulants and then the composite formulation. As far as testing of individual gases is concerned, no candidates for possible deletion from the proposed list can be indicated. The selection of sub-groups can be made on the basis of probable or known interaction of components, common sources, or simplification of sampling or analytical procedures. The first of these involves low-concentration, gas-phase reaction kinetics in the presence of ultraviolet light and may include ozone, hydrocarbons, and oxides of nitrogen. Sulfur dioxide, ozone, and oxides of nitrogen provide another candidate sub-group. Automobile exhaust components are typical of a common source sub-group and may include hydrocarbons, aldehydes, oxides of nitrogen, carbon monoxide, and carbon dioxide. Sub-groups may also be chosen which produce the least amount of interference in the analytical procedures, or, because of their relative concentrations, allow a simple sampling procedure.

Subsequently, the dry particulate formulation will be tested separately and in conjunction with the gaseous components.

The techniques to be described have been selected for their simplicity and manageability as well as from cognizance of the rigid safety program which is patently related to the prime test function. A considerable amount of manipulatory detail must be involved in the gas injection methods. It was thought advisable, therefore, to choose techniques for injection of particulate and vaporizable components of the test formulation which involved little or no manipulation during injection. In so doing, the burden of manipulation effort has been shifted to the preparatory phases. Thus the over-all effort immediately associated with the injection of the total formulation is held to a minimum.

II Proposed Gas and Vapor Formulation

Seventeen gaseous and vaporizable compounds proposed for use in the test chamber are listed in Table D-I. The concentration of each is representative of the average maximum value found in the atmosphere over metropolitan areas. (See Appendixes A and B.) In columns 6 and 7 of Table D-I is given the theoretical quantity of each component necessary to produce the desired concentration in a 2.0 x 10^4-liter chamber at the conditions specified (20°C, 758.6 mm Hg). Sulfur trioxide is considered to be present as sulfuric acid. All other components are fed to the test chamber in the form listed, with the exception of ozone, which must be injected as a volumetric fraction of an oxygen stream.

III Gas and Vapor Injection Equipment and Techniques

A. Gaseous Components

1. Equipment

The equipment for injection of cylinder gas and generated gas into a static test chamber held at small negative pressure is shown schematically in Figure D-1. Specifications are given in the Figure D-1 legend, as are sources of supply, and will not be repeated. The equipment is envisioned as being mounted on a caster-wheel-equipped, two-deck table with a panel equal to table length mounted vertically on the top deck. Glass tubing, flasks, syringes, flow meters, and small lecture size gas bottles are mounted on the panel, and the larger gas cylinders and ozone generator are mounted on the lower deck. The overall length of the table will be about 7 ft, assuming component distribution suited to convenient manipulation of controls and syringes. The equipment table can be rolled to the test chamber. The manifold which acts as gas receptor* and sweep-gas channel, can be temporarily connected to the test chamber with the ball and socket joint shown in Figure D-1. After the injection procedure is completed, the equipment can be disconnected and moved away from the immediate vicinity of the test chamber.

All panel components are rigidly mounted, with suitable holes cut in the panel to permit alignment of connecting lines with a minimum of bends and couplings. Gas cylinders, generator flask (HCN), and bubblers should be capable of being decoupled and removed with ease. The syringes should be coupled to side ports on the glass gas-reservoirs with glass-to-glass seals and clamped, with convenient separation from the panel. The volumetric scales, of course, must be clearly and conveniently visible.

Regulator valving on gas cylinders carried on the lower deck of the table should be provided with extensions to permit convenient adjustment of gas flows.

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* Volume about 1 liter

Table D-I

GASEOUS TEST-FORMULATION

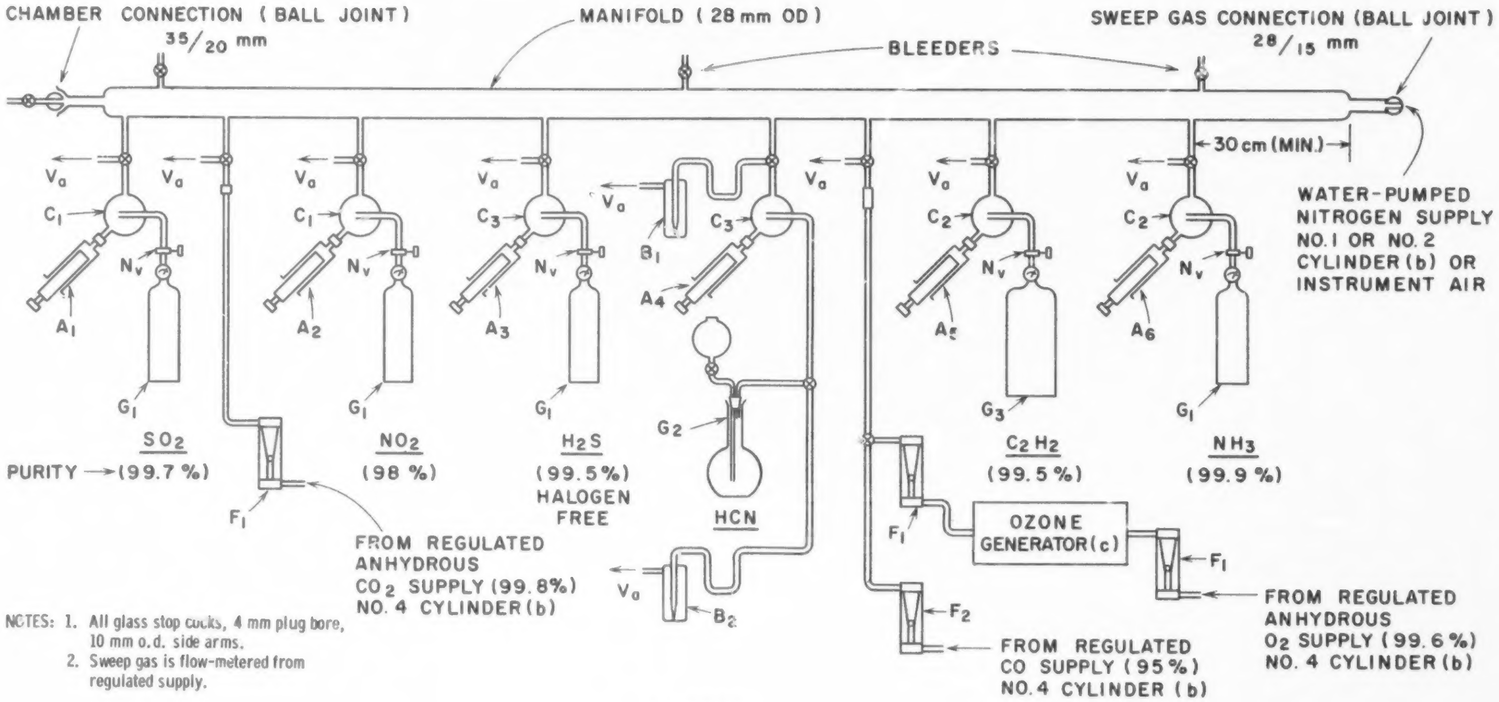
			Theoretical Concentration(a)		Theoretical Feed Total Component Per 2×10^4 Liters(b)	
Component	Source	Mole Weight	Volume (ppm)	Weight (ppm)	Volume (cc)	Weight (mg)
Sulfur dioxide	Cylinder	64.06	1.0	2.2	20.0	
Sulfur trioxide	(c)	80.06	0.05			3.3 (H_2SO_4)
Hydrogen sulfide	Cylinder	34.08	0.2	0.24	4.0	
Nitrogen dioxide	Cylinder	46.01	0.9	1.43	18.0	
Ammonia	Cylinder	17.03	0.3	0.18	6.0	
Formaldehyde		30.03	0.3	0.31		7.5
Acetaldehyde		44.05	0.1	0.15		3.7
Acrolein		56.06	0.1	0.19		4.7
Acetylene	Cylinder	26.04	0.55	0.50	11.0	
Hexane-n		86.17	0.28	0.83		20.1
Benzene		78.11	0.27	0.71		17.0
Carbon monoxide	Cylinder	28.01	10.0	9.66	200.0	
Carbon dioxide	Cylinder	44.01	400.0	607.6	2000.0(d)	
Ozone	High voltage discharge	48.00	0.2	0.33	4.0	
Hydrogen fluoride	35% hydrofluoric acid	20.01	0.008	0.006	0.16	0.15
Acetic acid		60.05	0.2	0.42		9.98
Hydrogen cyanide	$Ca(CN)_2$+ H_2SO_4	27.03	0.1	0.07	2.0	

(a) At test chamber conditions which were assumed to be 20°C at 758.6 mm Hg (0°C). Dry air was assumed to have a molecular wt of 28.97.

(b) Chamber volume taken as equivalent to 2.406×10^4 gm dry air per conditions of note (a).

(c) Included with particulate formulation since injection is accomplished by thermally induced bursting of glass ampule charged with 0.01 M H_2SO_4 solution

(d) Volume added is in excess of the 300 ppm (vol) taken as typical atmospheric concentration


CHAMBER CONNECTION (BALL JOINT)
35/20 mm
MANIFOLD (28 mm OD)
BLEEDERS
SWEEP GAS CONNECTION (BALL JOINT)
28/15 mm
30 cm (MIN.)
WATER-PUMPED NITROGEN SUPPLY NO. 1 OR NO. 2 CYLINDER (b) OR INSTRUMENT AIR
V_a
C_1
C_2
C_3
N_v
A_1
A_2
A_3
A_4
A_5
A_6
B_1
B_2
G_1
G_2
G_3
F_1
F_2
SO_2
PURITY → (99.7 %)
NO_2
(98 %)
H_2S
(99.5%) HALOGEN FREE
HCN
C_2H_2
(99.5 %)
NH_3
(99.9 %)
OZONE GENERATOR (c)
FROM REGULATED ANHYDROUS CO_2 SUPPLY (99.8%) NO. 4 CYLINDER (b)
FROM REGULATED CO SUPPLY (95%) NO. 4 CYLINDER (b)
FROM REGULATED ANHYDROUS O_2 SUPPLY (99.6%) NO. 4 CYLINDER (b)

NOTES: 1. All glass stop cocks, 4 mm plug bore, 10 mm o.d. side arms.
2. Sweep gas is flow-metered from regulated supply.

LEGEND

A_1 = 30 cc B-D Yale hypodermil syringe (a)
A_2 = A_5 = 20 cc B-D Yale hypodermil syringe (a)
A_3 = A_6 = 10 cc B-D Yale hypodermil syringe (a)
A_4 = 5 cc B-D Yale hypodermil syringe (a)
B = Water bubbler (B_1 = 50 cc, B_2 = 100 cc)
C = Spherical chamber (C_1 = 200 cc, C_2 = 100 cc, C_3 = 50 cc)
F_1 = No. 203 flow meter tube stainless steel float (b)
F_2 = No. 202 flow meter tube stainless steel float (b)

G_1 = Lecture bottle (b)
G_2 = Ca(CN) hydrogen cyanide generator (100 cc)
G_3 = No. 4 cylinder (b)
N_v = Appropriate needle valve (b)
V_a = Vent to atmosphere (capillary restricted or water bubbler with series U-tube)
(a) Any scientific or medical supply house
(b) Matheson Chemical Co., Inc., East Rutherford, N. J. (catalogue dated March, 1956)
(c) Ozone Processes Div. Welsbach Corp., 1500 Walnut St., Philadelphia, Pa.

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FIG. D-1

SCHEMATIC OF GAS INJECTION SYSTEM

Control of sweep-gas flow duration could be made semi-automatic by incorporation of an electromagnetic valve* in the supply line. The valve-open cycle could be automatically timed by a motor-driven cam and micro-switch** which could be actuated by a push-button type, momentary contact switch located at the test chamber end of the table. A thirty-second flow duration of sweep-gas through the manifold at the rate of 10 liters per minute will provide ample gas sweep from the (25 mm i.d.) manifold into the test chamber. The sweep-gas control system should also be capable of "continuous-on" operation at 5 liters per minute during the metered injection of CO_2, CO, and O_3***.

A bubbler in the vent-to-atmosphere line is shown in Figure D-1 only on the HCN reservoir. It may be convenient for visual control of flow from gas cylinders to reservoirs of the other gas manipulation facilities to provide a bubbler for each vent-to-atmosphere line. With reasonable care the u-tube traps shown in the HCN vent line should be adequate to prevent possible back flow of water from the bubblers to the gas reservoir or generator flask.

2. Procedure

Gases metered by mechanical displacement with hypodermic syringes include SO_2, NO_2, H_2S, HCN, C_2H_2, and NH_3. With the exception of HCN, which is chemically generated, all are supplied from small, pressurized gas cylinders. The metering procedure for all is approximately the same.

The manifold is connected to the test chamber (the intervening gas valve is closed and the test chamber is static and initially at a negative pressure of 2 in. of water). The manifold is bled to atmospheric pressure and then all bleeder valves are closed. The three-way cock between spherical glass reservoir and manifold is set to connect the reservoir with vent-to-atmosphere (through a water bubbler if desired). The hypodermic syringe piston (properly sealed with a minimum quantity of silicone grease) is set at zero volume. The gas cylinder needle valve is opened slowly and the gas is allowed to flush the reservoir. From 50 to 70 seconds, depending on the size of the reservoir, (see C_1, C_2, C_3 of Figure D-1 legend), should be sufficient to accomplish the reservoir flush. With the gas still flowing slowly through the reservoir, the hypodermic piston is positioned slowly to the desired volume of gas.* The gas cylinder needle valve is closed. The three-way cock is positioned, after a short time interval to allow pressure stabilization, to connect the gas reservoir with the manifold. The hypodermic piston is brought slowly to zero syringe volume to prevent excessive pressure change as gas flows from reservoir through the 4-mm cock to the manifold. The manifold has a volume of about a liter; therefore, the pressure change due to addition of the gas will be 0.05% or less, depending on the gas being injected. The three-way cock between reservoir and manifold is then closed. The gas-valve to test chamber is opened. Gas-sweep through the manifold at the rate of 10 liters/min is started and continued for 30 seconds. The test chamber gas valve is closed and the next metering operation is performed.

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* General Controls Co.,Skokie,Ill. Type K-10A, 3/8 in.ips, 0.25 in. port, No. 225 Solenoid,Class "A" coil, 115v/60 cycles,air at 60-80°F

** R.W. Cramer Co.,Inc. Type 320 automatic-reset interval timer (60 sec) available through L.G.White & Co., 8041 Colesville Rd.,Silver Springs,Md.

***Ozone will be contained to the extent of $\sim$0.1 volume percent in an O_2 stream flowing at the rate of 2 to 3 liters/min through the ozone generator (see ozone generation procedure below)

Generation of HCN gas is accomplished by inserting approximately 0.02 mole of $Ca(CN)_2$ in the generator flask. Two to three ml of dilute acid are added from the small separatory funnel. Reservoir flushing with gas should be allowed to continue for 80 to 90 seconds before beginning the metering procedure. When the hypodermic syringe has been set at the desired volume, the three-way cock immediately downstream from the generator should be used to divert the excess gas to the secondary bubbler. Injection of HCN gas into the manifold is accomplished as described above.**

The metered flow of CO_2 at 0.5 liter/min is begun with sweep-gas flow set at 5 liter/min (continuous) and continued for 4.1 min with the test chamber gas valve open. The three-way cock at the manifold is set at the conclusion of the timed flow to vent the CO_2 supply line to the atmosphere followed by shut-down of the CO_2 supply. Injection of CO is accomplished in a similar fashion at a flowrate of 50 ml/min for 4.1 min.***

After CO injection the three-way cock immediately downstream from the CO flow meter is positioned to connect the O_3-O_2 flow meter to the line which is vented to the atmosphere through the three-way cock nearest the manifold. The oxygen flow through the ozone generator is adjusted at the rate of 2.8 liters/min. The high voltage supply is adjusted so that 0.1 percent (by vol) of ozone is being generated in the O_2 stream.* The stream is then turned into the manifold with the test chamber gas valve open and allowed to continue for 1.5 min. Manifold gas-sweep is set at 5 liters/min. Vent supply line to atmosphere at conclusion of the timed flow. Then shut down ozone generator and O_2 gas stream.

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* To allow for losses due to wall adsorption, efficiency of manifold gas-sweep, and sampling of test chamber atmosphere, from 5-10 percent in excess of the theoretical quantities listed in Table C-IX will have to be metered. The exact amount of excess will be determined by test.

** In view of the toxicity of HCN gas to humans and its lack of bactericidal properties reported by Fairhall (see reference at end of Appendix D), omission of HCN from the proposed test formulation may be desirable.

*** It is desirable to bleed and flush the manifold after each injection.

This completes the gas injection. The manifold can be disconnected following closure of the test chamber gas valve and the table removed from the test area.

3. Specifications for Ozone Generator

The T-23 laboratory ozonator** has a rated capacity of 3 g of ozone/hr with dry air and 6 g with dry oxygen, based on an ozone concentration of 1 percent by wt with dry air or 2 percent by wt with dry oxygen. Concentrations up to 6 percent can readily be obtained by reducing the gas flow, but at some loss in output.

Alternating current at 115 v, 60 cycles is required. Power consumption is 60 watts. Standard equipment comprises: high voltage transformer, voltage regulator, voltmeter, circuit breaker, air or oxygen pressure maintaining valve, throttling valve, sampling valve, pressure gauge, pressure relief valve and flowmeter -- all mounted integrally within the cabinet and completely wired and piped with fittings for gases and cooling water. Connections may be made with laboratory tubing.

Clean, dry air or oxygen must be supplied at -60°F dew point at a rate of about 0.1 standard cfm and at about 10 psig pressure to obtain rated capacity. Cooling water at a maximum temperature of 80°F at a rate of 5 gal/hr is also required. The dimensions of the ozonator are: 1 ft 7 in. by 1 ft 3 in. by 3 ft 3 in.; the shipping weight, 270 lb.

The Welsback T-23 sells for $1200 fob Philadelphia, and is available for shipment within 10 days of receipt of order. Each T-23 is shipped in a special returnable container on which there is a deposit of $150.

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* According to the manufacturer's instructions for high-voltage generator.

** The Welsbach Corp., Ozone Processes Div., 1500 Walnut St., Philadelphia 2, Pa.

B. Vaporizable Components

1. Preparation

It is proposed that vaporizable components (excepting hydrofluoric acid) be dispersed within the test chamber from vapor-pressurized glass ampules as well as by open liquid evaporation in conjunction with a heat source. This technique requires no further manipulation once it is set up in the chamber.

Aqueous solutions of the components having high vapor pressure are made up as stock solutions at the molar concentrations shown in Table D-II. The volumes of these solutions containing the weight of components necessary to charge the chamber with the desired air concentration are accurately measured into thin-walled glass ampules. The low boiling liquids (n-hexane and benzene), being of small volume, are reserved for open evaporation.

2. Equipment

Five-ml glass ampules must be fabricated in the glass blowing shop to the following dimensions: 18 mm o.d., 16-17 mm i.d., and 35 mm measured from ampule base to shoulder. Testing with a 3-ml liquid charge will reveal best geometry of shoulder and tip to guarantee bursting under the conditions specified below. Three of these are required for the large volume (2.93- to 3.57-ml) solutions, as indicated in Table D-II.

A brass block machined and drilled to the dimensions shown in Figure D-2 serves as a holder for the ampules. The two shallow cavities shown are for the evaporation of small liquid volumes (n-hexane and benzene) and are sufficiently separated from the ampule cavities to prevent their contents from being disturbed when the ampules explode. In addition to serving as an ampule and liquid holder, the brass block also provides for proper heat distribution.

The heat source is an electric hotplate.* The hotplate, when operated at the high output setting, will produce a temperature of 400°C in the brass block cavities in about 20 min. This should be sufficient to assure bursting of the ampules a reasonable length of time after power is applied to the hotplate.

Equipment for injection of the 0.01 M hydrofluoric acid solution shown in Figure D-3 is an all-glass aspirating-type disperser fabricated from Pyrex glass according to the dimensions shown. At the concentration specified the loss due to reaction with the glass will be very much smaller than adsorption losses within the chamber itself.

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* Edwin L. Wiegand, Pittsburgh,Pa., Type ROPH 7120 Chromalox hotplate, 120v/60 cycles,1200 w. Available from any laboratory equipment jobber.

Table D-II

STOCK SOLUTION CONCENTRATIONS AND THEORETICAL CHARGING VOLUMES OF VAPORIZABLE COMPONENTS

Compound	Molarity of Stock Solution	Liquid Density (gm/ml)(20/40°C)	Theoretical Liquid Volume (ml)
Formaldehyde	0.2		1.25
Acetaldehyde	0.1		0.84
Acrolein	0.1		0.84
TOTAL			2.93(a)
n-Hexane		6.84×10^{-1}	0.0294(b)
Benzene		8.794×10^{-1}	0.0194(b)
Hydrofluoric acid	0.01		0.75(c)
Acetic acid	0.05		3.33(a)
Sulfuric acid	0.01		3.37(a)

(a) Volume is charged into ~5-ml, thin-walled, glass (soft) ampules which must be laboratory fabricated to measure 18 mm o.d., 16-17 mm i.d., and 35 mm from base to shoulder. Use certified pipettes.

(b) Use appropriate sizes of certified lambda transfer pipettes (available from Wakefield Industries, Inc., Div. of Radiation Counter Labs., Inc., 5108 W. Grove, Skokie, Ill.) to charge small cavities in brass hot-block.

(c) The volume of solution necessary to achieve the desired concentration of HF in the chamber atmosphere (8 ppb by vol) must be determined by test, since it is not possible to predict losses due to adsorption on surfaces exposed to chamber atmosphere.

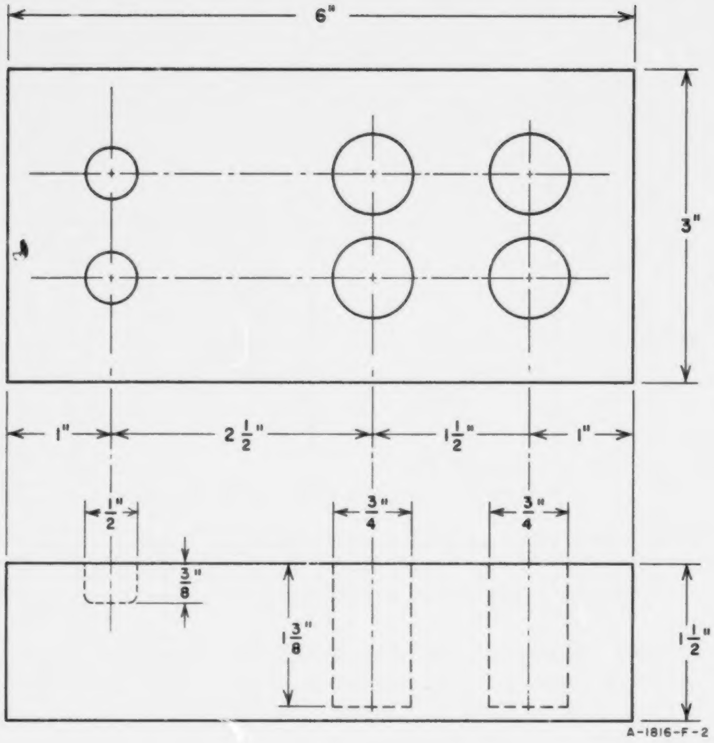
6"
3"
1"
2 1/2"
1 1/2"
1"
1/2"
3/4"
3/4"
3/8"
1 3/8"
1 1/2"
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FIG. D-2

BRASS AMPULE AND LIQUID HOLDER

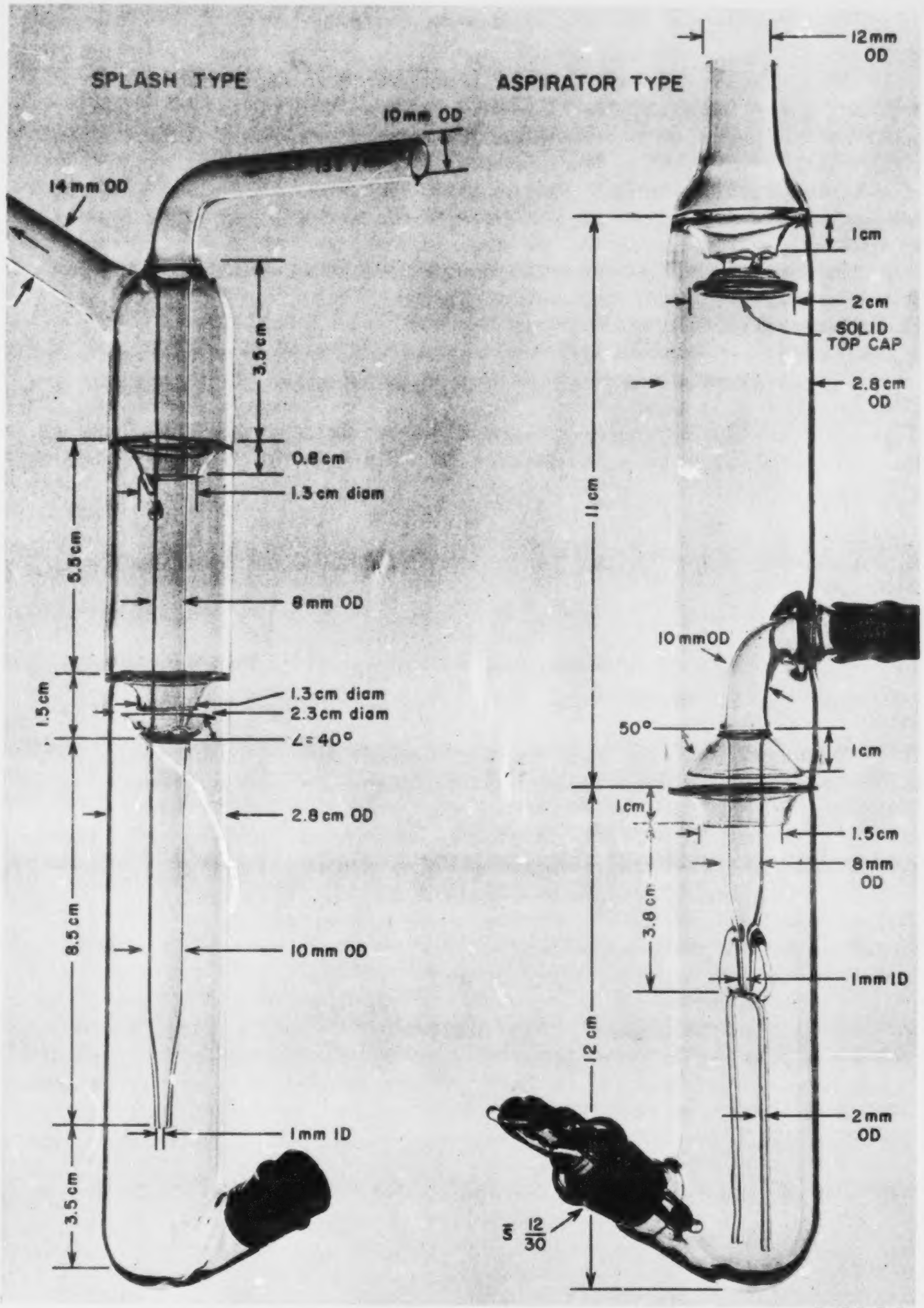
SPLASH TYPE
ASPIRATOR TYPE
10mm OD
14 mm OD
3.5 cm
0.8 cm
1.3 cm diam
5.5 cm
8mm OD
1.5 cm
1.3 cm diam
2.3 cm diam
∠=40°
2.8 cm OD
8.5 cm
10 mm OD
1 mm ID
3.5 cm
12mm OD
1cm
2 cm
SOLID TOP CAP
2.8 cm OD
11 cm
10 mmOD
50°
1cm
1cm
1.5cm
8mm OD
3.8 cm
1mm ID
12 cm
2mm OD
$ 12/30
P-1816-F-3

FIG. D-3

LIQUID AEROSOL DISPENSERS

3. Procedure

The ampules containing the aldehyde mixture, acetic acid, and sulfuric acid are inserted in the deep cavities in the brass hot block. Three hundred lambdas of n-hexane and 200 lambdas of benzene are pipetted into the shallow cavities. The block is placed on the hotplate in the test chamber. Application of power to the hotplate is deferred until the gas injection procedure is begun. The latter will require about thirty minutes, which should allow ample time for ampule vapor pressures to reach the magnitude necessary to assure bursting. About 2000 Btu will be added to the sensible heat of the chamber air, not counting losses to the walls during 30 min.

The aspirating-type disperser is mounted to feed directly into the chamber at a point where it will become involved in rising air from the circulating fan. The disperser will require about 15 liters/min at approximately 8 psig to deliver roughly 0.5 ml/min. Duration of feed must be determined by test since it is not possible to predict how much will be lost by adsorption on the chamber walls before the desired concentration of 8 ppb (vol) is achieved.

IV Particulate Injection Equipment and Techniques

A. Non-liquid Components

1. Preparation

Twenty-three chemical compounds which are typical of the solid aerosol comprising atmospheric contamination are proposed for the test chamber formulation. These are listed in Table D-III with individual weights in μg/cu m. The producer of each component is also listed, as determined from the Chemical Materials Catalogue and Producers Directory for 1955-56 published by Reinhold Publishing Corp. The majority of the chemicals listed are available as reagent grade chemicals having a minimum of contaminants.*

Each of the components (with the exception of water solubles) must be ball-milled to a mass median diameter of 0.5 to 1.0μ, using a sample size appropriate to optimum ball mill performance. Procurement of reagent grade chemicals in powdered form will minimize ball mill time when milling is necessary.

Each chemical component is accurately weighed to an amount equivalent to 10^5 times its desired unit concentration in the test

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* The number of water soluble chemicals chosen for the test formulation was limited by the necessity for utilizing industrially related and natural earth compounds as well as adherence to a specified ash weight. (Table VII, Progress Report No. 4).

Table D-III

PARTICULATE TEST-FORMULATION

Prime Component	Chemical Component	Weight Chemical (μg/cu m)	Molecular Weight	Specific Gravity	Estimated Ash Wt (μg)	Producers
Al	$Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$ (china clay)	40.9	258.09	2.60-2.63	35.17	Georgia Kaolin Co., 514 Pennsylvania Ave., Elizabeth, N.J. 100% $< 2\mu$
	$CaO \cdot Al_2O_3 \cdot 2SiO_2$ (lime feldspar)	35.1	278.14	2.70-2.76	35.1	International Minerals & Chemical Corp., 20 N. Wacker Dr., Chicago 6, Ill.
	$Na_2Al_2(SO_4)_4$ $24H_2O$*	17.0	916.56	1.68	3.99	General Chem. Div., Allied Chem & Dye Corp., 40 Rector St. New York 6, N.Y.
As	As_2O_3*	0.07	177.82	3.86	0.07	" " " "
Ba*	(see Zn)	--			--	
Be	Be F_2	0.05	47.02	1.99	0.03	" " " "
Bi	Bi_2O_3*	0.10	466.00	5.60	0.18	" " " "
C	(Lamp black)	300.0	--	1.77	--	Monsanto Chem. Co., 1700 S. Second St., St. Louis 4, Mo. (Grade No. 1)
Ca	$CaCO_3$*	1.40	100.09	2.71	0.78	J.T. Baker Chem. Co., Phillipsburg, N.J.
	CaF_2*	0.60	78.08	2.97-3.25	0.60	" " " "
	$CaSO_4 \cdot 2H_2O$*	55.8	172.17	2.31-2.33	44.14	" " " "
Cd	CdO*	0.06	128.41	6.95-8.15	--	" " " "
Co	Co_2O_3*	0.02	165.88	5.18	0.02	" " " "
Cr	Cr_2O_3*	0.02	152.02	5.21	0.02	Baker & Adamson, Gen. Chemical 40 Rector St., New York 6, N.Y.
Cu	$CuSO_4 \cdot 5H_2O$*	3.90	249.71	2.56	1.24	J.T. Baker Chem. Co., Phillipsburg, N.J.
Fe	Fe_2O_3*	14.3	159.68	4.9-5.3	14.3	" " " "
	Fe(metal powder)	0.8	--	7.86	1.03	" " " "

Table D-III (Cont'd.)

Prime Component	Chemical Component	Weight Chemical (μg/cu m)	Molecular Weight	Specific Gravity	Estimated Ash Wt (μg)	Producers
Hg	$HgCl_2$*	0.28	271.52	5.44	--	Baker & Adamson, Gen.Chem.Div. 40 Rector St., New York 6, N.Y.
K	K_2SO_4*	19.1	174.25	2.66	10.31	J.T.Baker Chem.Co., Phillipsburg, N.J.
Mg	$MgSO_4 \cdot 7H_2O$*	40.0	246.49	1.64-1.68	19.5	" " " "
	$3MgO \cdot 4SiO_2 \cdot H_2O$	21.0	379.22	2.70-2.80	20.0	Celkate-Johns-Manville Corp. Celite Div., 22 E.40th St., New York 6, N.Y.
Mn	MnO_2*	0.09	86.93	5.03	0.09	J.T.Baker Chem.Co., Phillipsburg, N.J.
Mo	MoS_2	0.15	160.07	4.80	0.15	Acheson Colloids Co., Port Huron, Mich.
Na	NaCl*	6.04	58.45	2.02	6.04	J.T.Baker Chem.Co., Phillipsburg, N.J.
	$Na_2SO_4 \cdot 10H_2O$*	20.1	322.22	1.46	10.65	" " " "
	$NaNO_3$*	13.7	85.01	2.26	6.26	" " " "
Pt	PbO*	3.2	223.21	8.0	3.2	" " " "
	$PbSO_4$*	2.1	303.27	6.2	2.1	" " " "
Sb	Sb_2O_3*	0.72	291.52	3.74-4.15	0.72	" " " "
Sn	SnO*	0.16	134.70	6.44	0.16	" " " "
Ti	TiO_2*	0.15	79.90	3.84	0.15	" " " "
	$MgO \cdot TiO_2 \cdot SiO_2$ (Magnesium titanate)	3.0	180.28		3.0	Titanium Alloy Mfg.Div., National Lead, 111 Broadway, New York, N.Y.
V	V_2O_5	0.16	181.90	3.36	0.16	Harshaw Chem.Co., 1945 E.97th St., Cleveland 6, O.
W	$CaWO_4$(scheelite)	0.47	288.00	5.88-6.14	0.47	Electro Metallurgical Co., Div. of Union Carbide & Carbon, 30 E. 42nd St., New York 17, N.Y.

Table D-III (Cont'd.)

Component	Component	Weight Chemical (μg/cu m)	Molecular Weight	Specific Gravity	Estimated Ash Wt (μg)	Producers
Zn	ZnO*	2.50	81.38	5.61	--	J.T.Baker Chem.Co.,Phillipsburg, N.J.
	30% ZnS 70% $BaSO_4$(lithopone pigment)	0.4	--	4.30	0.28	New Jersey Zinc Co.,160 Front St., New York 38, N.Y.
TOTAL		603.34			226.37	
	H_2SO_4	165.0	(0.137 ppm wt)			
	Free SiO_2	20.0				
	Organics**	30.0				
Total Particulate		818.34				
Total Combustible***		571.97				

Formulation includes:

Cl^-	3.72 μg/cu m
NO_3^-	10.0 μg/cu m
F^-	0.34 μg/cu m
$SO_4^=$	162.0 μg/cu m

* Reagent grade chemicals

** Assumed to be oil aerosol composed of 60% spent crankcase oil and 40% diesel oil

*** 818.34 - (226.37 + 20.0) = 571.97

atmosphere. Thus the components present in the smallest fraction (Co_2O_3 and Cr_2O_3) can be weighed in the amounts of 20 mg to 0.2 mg accuracy. The components are all added to 2 liters of water containing 0.1 percent of an appropriate wetting agent such as Aerosol OT.* This will be the stock solution suspension from which aliquots are taken.**

Free silica is not included in the formulation as is indicated in Table D-III, since it is expected that free silica will be introduced into the test atmosphere from the explosive bursting of glass ampules.

2. Equipment

Five-ml ampules, as described in Section III-B-2, are used to receive a 3-ml charge of an aliquot of the above stock solution.

3. Procedure

While the stock solution is being mechanically stirred to assure uniform distribution of suspensoids, a 10-ml aliquot is withdrawn slowly with a transfer pipette. This aliquot is diluted with water to 1-liter volume using part of the water to rinse the pipette. A 10-ml aliquot is withdrawn from this well-stirred solution-suspension with a transfer pipette and diluted to a volume of 150 ml, a part of the water being used to rinse the pipette. A 3-ml sample of the resulting mixture is transferred by pipette to the 5-ml ampule, which is then sealed.

The ampule is placed in the brass block (Figure D-2) cavity remaining after insertion of the ampules containing vaporizable components. The block is set on the hotplate in the chamber and power applied when the chamber is ready for gas injection. The bursting of the ampule in deep cavitation will impart sufficient dispersal speed to the water suspension that little agglomeration of particulate is expected to occur.

B. Liquid Aerosol Component

1. Preparation

Filter 100 ml of used crankcase oil and mix with 67 ml of diesel fuel oil to make stock solution.

---

* American Cyanamid Co., Indust. Chem. Div., 30 Rockerfeller Plaza, New York 20, N.Y.

** The stock solution may be assayed to test the accuracy of the formulation and the representativeness of liquid aliquots, which must be taken while stock solution is being amply stirred.

2. Equipment

The jet-type disperser shown in Figure D-3 is arranged to operate with about 4 to 6 psig and to inject the aerosol stream directly into the test chamber so that the stream is ultimately mixed with vertically moving air currents.

3. Procedure

Fill the reservoir space of the disperser with about 10 ml of the oil mixture. Weigh the charge dispersed with an accuracy of ±0.2 mg. Time operation of disperser to pre-tested duration so that approximately 0.6 mg of the oil mixture is injected.

Reference

Fairhall, L. T. Industrial Toxicology - Hydrogen Cyanide and Other Cyanides. Indust. Hyg. News Letter 11(2), 29 (1951)

Appendix E

SAMPLING AND ANALYTICAL PROCEDURES

The sampling and consequent analytical procedures were chosen for the particular problem of testing static atmospheres with bacteria. Emphasis has been placed upon simplicity of sampling and of analysis; although definite procedures are established, alternative methods are given for freedom of operation.

The sampling equipment consists principally of the Greenburg-Smith impinger, preceded by a millipore filter for the collection and removal of solids and bacteria from the gas stream. A critical orifice is used to measure the rate of air flow.

Two (or more) techniques are given as analytical procedures for each type of component. At least one procedure is suggested for an accurate determination of the amounts of material collected, and another method is suggested as more rapid but less accurate.

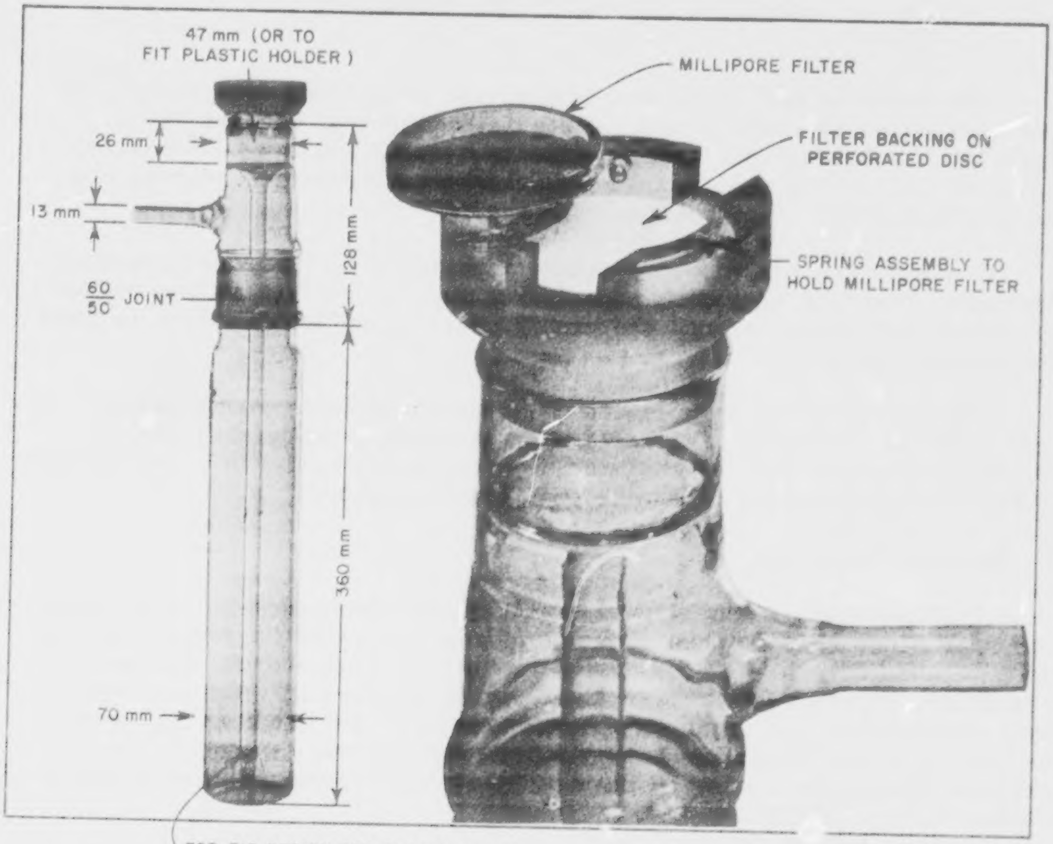
I Sampling Equipment

The fundamental sampling apparatus is the Greenburg-Smith impinger, the dimensions of which are shown in Figure E-1. The large impinger is used because several gaseous components can be analyzed on the same absorbent. However, a smaller impinger may be used if only one component is analyzed per impinger; the advantage of the smaller impingers is that they are readily obtainable from any laboratory supply house, whereas the larger impingers must be specially ordered and individually made.

A millipore filter holder and paper precede the Greenburg-Smith impinger (see Figure E-1).

A thermometer and vacuum gage should follow the impinger. These may be placed in the top of a flask which would serve as a safety catch-all for any solution leaving the impinger. Temperature and pressure measurements are taken to correct the gas flow rate to standard conditions. As at this point the sampled gas is saturated with moisture, the above measurements may be neglected if after a number of tests it is found that conditions are sufficiently constant so that a common factor may be used for temperature, pressure, and humidity corrections.

A critical orifice may be used to estimate the gas flow rate. For convenience the orifice is placed after the safety catch bottle. The critical orifice is calibrated for the desired flow rate; house vacuum is used in conjunction with a vacuum gage after the critical orifice to make certain that sufficient pressure is available for the orifice to function properly.


47 mm (OR TO FIT PLASTIC HOLDER)
26 mm
13 mm
60/50 JOINT
128 mm
360 mm
70 mm
MILLIPORE FILTER
FILTER BACKING ON PERFORATED DISC
SPRING ASSEMBLY TO HOLD MILLIPORE FILTER

FOR TIP DESIGN SEE PUBLIC HEALTH
BULLETIN NO. 217, PUBLIC HEALTH
REPORT 52 NO. 33 — AUGUST 13, 1937.

P-1816-F-4

FIG. E-1

GREENBERG-SMITH IMPINGER WITH MILLIPORE FILTER

References to sampling and analytical techniques may be found in many literature references (1,2,3,4,5).

II Analytical Procedures

It is contemplated that each component will be initially prepared in the test chamber to check the addition procedure as well as the sampling and analytical procedures. After all steps in the above operations have been checked and rechecked, it is then envisioned that the simulant bacteria will be tested.

The first sampling techniques should, in the case of ammonia, use at least two impingers -- one with the millipore holder and paper preceding the impinger and the second without the millipore filter. The analysis of the impinger solutions should be made by either the ammonia distillation method or the Folin-Nessler reagent. The purpose of the above sampling and analysis is to determine whether there is adsorption of the gaseous component, ammonia, on the millipore paper and holder.

Simultaneously with the above tests, a third sampling and analysis method should be tested. In the case of ammonia, the simple bubbler method is suggested. The results of the rapid but less accurate bubbler method are then compared with the results of the more accurate but time-consuming methods.

After tests have satisfactorily calibrated the gross method against the accurate method, future tests using bacteria will be undertaken. To minimize the analytical effort during bacteria tests, only the rapid or gross method could be used.

Other individual gaseous components should be treated in like manner. Table E-I lists the sampling and analytical schematic for the proposed tests.

A. Ammonia

Ammonia is collected in a Greenburg-Smith impinger containing 0.05 N H_2SO_4. The resultant solution is analyzed accurately by either the ammonia distillation method or the Folin-Nessler method; analytical procedures follow.

The rapid method of analysis for ammonia was described by Gisclard, et al. (6) and consists of a simple bubbler containing 0.0001 N H_2SO_4 and methyl purple indicator. The time required for the bubbler to change color depends upon the ammonia concentration in the gas stream.

Table E-I

SAMPLING AND ANALYTICAL SCHEMATIC

Component	Theoretical Concentration (ppm by vol)	Weight/cu ft (μg)	Sampling Method	Analytical Method
Ammonia	0.3	6.4	Impinger, 100 ml 0.05 NH_2SO_4 5 min sampling period at 1 cfm-32.0 μg NH_3	Ammonia distillation Folin-Nessler method Simple bubbler method
Aldehydes	0.5	17.7	Impinger, 100 ml 1% $NaHSO_3$ 5 min sampling period at 1 cfm-58.5 μg HCHO	Titration of bisulfite soln. Polarographic method Phenylhydrazine hydrochloride method
Acids, as CH_3COOH	0.8	60.6	50 ml aliquot 181.8 μg CH_3COOH Impinger, 500 ml, 30 min sampling at 1 cfm	Potentiometric titration Fleisher's methyl purple indicator
Fluorides, as HF	0.008	0.2	350 ml aliquot 6.3 μg HF	Distillation-thorium nitrate titration Ion exchange-thorium nitrate titration
Carbon dioxide	400.0	21,600.0	50 ml aliquot 64.8 mg CO_2	Carbon dioxide evolution Direct titration
Sulfur dioxide	1.0	81.0	50 ml aliquot 40.5 μg SO_2 Impinger, 500 ml, 5 min sampling at 1 cfm	Gravimetrically Polarographically Iodometrically Colorimetrically
Oxides of nitrogen	0.9	52.4	50 ml aliquot 26.2 μg NO_2	Phenoldisulfonic method Saltzman's reagent

Table E-I (Cont'd.)

Component	Theoretical Concentration (ppm by vol)	Weight/cu ft (μg)	Sampling Method	Analytical Method
Hydrochloric acid	0.2	9.5	100 ml aliquot) Impinger, 9.5 μg HCl) 500 ml,) 5 min	Amperometric titration Turbidimetric method
Hydrogen cyanide	0.1	3.4	100 ml aliquot) sampling 3.4 μg HCN) at 1 cfm	Amperometric titration Titration with silver nitrate
Sulfur trioxide	>0.05	>6.3	Millipore filter from SO_2 absorber- >31.5 μg SO_3	Turbidimetric method Miscellaneous methods
Hydrogen sulfide	0.2	8.6	100 ml ammonical $CdCl_2$ soln., 43.0 μg H_2S	Back titration method Instrumental method
Ozone	0.2	12.1	Acidified potassium iodide bubbler spray contactor	Direct titration Potentiometric titration
Carbon monoxide	10.0	354.0	Instrumental	Instrumental
Organics	1.1	120.0	Instrumental	Instrumental
Solids	740.0(a)			

(a) μg/cu m

ASM 7.01
AMMONIA
DISTILLATION
May 1, 1950

STANFORD RESEARCH INSTITUTE
ANALYTICAL SECTION METHOD

Determination of

AMMONIA IN ABSORBER SOLUTIONS
DISTILLATION METHOD

Scope

1. This method is intended for the determination of ammonia in dilute acid absorber solutions. Large concentrations of volatile amines, which steam distill from alkaline solutions, will interfere with the test.

Outline of Method

2. The acid absorber solution is transferred to a distillation flask and made strongly alkaline. The ammonia formed is distilled into a boric acid solution and titrated with standard acid using a mixed indicator.

Reagents

3. (a) Boric Acid, 3%. Dissolve 15 g. of c.p. boric acid crystals in 500 ml. of boiling water. Cool and transfer to a glass stoppered Pyrex bottle.

(b) Hydrochloric Acid, standard 0.02 N and 0.1 N.

(c) Indicator. Mix 10 ml. of 0.1% alcoholic bromcresol green with 2 ml. of 0.1% alcoholic methyl red.

(d) Sodium Hydroxide Solution. Dissolve 500 g. of sodium hydroxide pellets in 750 ml. of distilled water.

Apparatus

4. (a) Kjeldahl distillation apparatus, including 500 ml. Kjeldahl flasks.

(b) Erlenmeyer flasks, 500 ml.

(c) Burets, 10-, 25-, and 50-ml.

5. (a) Transfer the absorber solution or a known aliquot to a 500-ml. Kjeldahl flask and add distilled water to make a total volume of 300 ml. Add a few carborundum boiling chips to the flask.

(b) Place 50 ml. of boric acid solution in a 500-ml. Erlenmeyer flask. Add 3 drops of indicator and place under the condenser so that the tip of the condenser is just covered. Add 10 ml. of the sodium hydroxide solution to the Kjeldahl flask in such a way that two layers are formed. Quickly attach the flask to the distillation apparatus and swirl to mix the solution. Heat the contents of the flask rapidly to boiling and then adjust the flame so that the boiling is continuous but not too rapid. Note 1.

> Note 1. The danger of drawing some of the receiving acid back up into the condenser is minimized by bringing the liquid in the flask to boiling as quickly as possible and by adjusting the receiver so that the end of the condenser dips only slightly into the solution.

Continue the distillation until about 150 ml. of the liquid in the flask has been distilled over. Titrate with standard hydrochloric acid of appropriate strength. Note 2. Subtract the blank carried through in the same way.

> Note 2. If less than 0.5 milliequivalent of ammonia is expected in the titration, the standard 0.01 N acid should be used. If large amounts of ammonia are expected the aliquot taken for distillation should be such that less than 50 ml. of 0.1 N acid are required.

Calculation

6. Calculate the ammonia in the sample by means of the following equation:

$$\text{Ammonia, ppm} = \frac{(A-B)(N)(17.01)(1000)}{(W)}$$

where:

A = volume of standard acid used for sample,
B = ml. of standard acid used for blank,
N = normality of standard acid, and
W = weight of original sample in grams represented by the aliquot taken.

AMMONIA

Scope

1. This method is intended as an alternate for the distillation method.

Outline of Method

2. Ammonia is absorbed in sulfuric acid and determined colorimetrically by Nessler's method.

Reagents

3. Folin's Nessler Reagent*

a. After solution of 30 g of potassium iodide, 22.5 g of iodine, and 20 ml of water, add 30 g mercury to the 200-ml flask. Shake, until the iodine color disappears (7-15 minutes). When cooled, the solution will be greenish in color. The cooled solution is tested with starch iodide solution. Unless the starch test is positive, the solution may contain mercurous compounds and must be discarded. If the test is positive, decant the solution, washing the mercury and flask with water to a volume of 200 ml.

From this solution, prepare this final Nessler's solution as follows: to 662 ml of an accurately prepared 14.7 percent sodium hydroxide solution add 200 ml of the double iodide solution. Mix and allow to clear by standing.

b. The 14.7 percent sodium hydroxide solution may be prepared by dissolving 148 g sodium hydroxide in 148 ml of water. Filter through asbestos and without washing add 705 ml of water to the filtrate. The sodium hydroxide solution should be accurate to at least 5 percent.

c. Standard Ammonia Solution. Add 0.7868 g reagent grade ammonium sulfate to 0.1 N sulfuric acid and dilute to 1 liter. Dilute 10 ml of this solution to 100 ml with 0.1 N H_2SO_4.

Procedure

4. Colorimetric Calibration

Mix 1 ml of the Folin-Nessler reagent with each of the following calibration solutions and allow to stand 5 minutes for full color development.

---

* Jacobs, M. B., Chemical Analysis of Foods and Food Products, New York, 1938

ml std. NH_3 solution	ml 0.1 N H_2SO_4
0	10
0.5	9.5
1	9
2	8
4	6
6	4
8	2
10	0

The yellow color that appears is measured by a photoelectric colorimeter using a dark blue filter. The 100 percent transmission setting is referenced on 0.1 N H_2SO_4.

The results of the standard calibration, prepared for each new lot of reagents, are plotted on semi-log paper. The logarithmic scale is used for percent transmission and the linear scale for micrograms of ammonia (or directly into ppm NH_3 by volume for standard test solutions).

B. Aldehydes

The Golman and Yogoda (7) bisulfite method is recommended for aldehydes. In addition to the bisulfite method, procedures for the phenylhydrazine hydrochloride and the polarographic methods are also given.

The bisulfite method absorbs higher aldehydes much more slowly than formaldehyde. A slower sampling rate might be considered. Reynolds and Irwin (8) give an excellent review of basic methods of aldehyde analysis.

No rapid method is available for the analysis of aldehydes.

ASM 201.01
ALDEHYDES
BISULFITE
May 1, 1950

STANFORD RESEARCH INSTITUTE
ANALYTICAL SECTION METHOD

Determination of

ALDEHYDES IN SODIUM BISULFITE SOLUTIONS

Scope

1. This method is intended for the determination of aldehydes in gas streams after collection in sodium bisulfite scrubber solutions.

Outline of Method

2. Excess bisulfite in the absorbing solution is removed by addition of excess iodine. Excess iodine is removed by titration with thiosulfate solution. The resulting solution is chilled and the aldehyde-bisulfite complex broken down by addition of chilled buffer solution. The resulting bisulfite is titrated as a measure of aldehyde content.

Reagents

3. (a) Potassium Iodate, Standard 0.05 N. Dissolve 3.5670 g. of pure potassium iodate in distilled water and add 2 g. of sodium hydroxide pellets. Then add 10 g. of potassium iodide (free from potassium iodate). After complete solution of all salts, adjust to room temperature and dilute to 2 l. in a volumetric flask.

(b) Sodium Thiosulfate, 0.05 N. Dissolve about 25 g. of sodium thiosulfate pentahydrate in 2 l. of freshly boiled and cooled distilled water. Store in a clean Pyrex bottle. To standardize this solution, pipette 25 ml. of the standard potassium iodate solution into a 300-ml. Erlenmeyer flask. Add 200 ml. of water and 20 ml. of hydrochloric acid. Allow to stand 1 minute and then titrate with the thiosulfate solution. As the end point is approached, add 10 ml. of 0.2% starch solution. Titrate carefully until the solution is colorless. (The thiosulfate solution should be restandardized every 15 days).

(c) Starch Solution, 0.2%. Add cold aqueous suspension of 2 g. of soluble starch to 1 l. of boiling water. Cool to room temperature and store in a clean bottle.

(d) Iodine Solution, approx. 0.1 N. Dissolve 20-25 g. of pure potassium iodide in as little water as possible in a 1 l. bottle. Add

12.7 g. of iodine and shake the contents of the bottle until all the iodine is dissolved. Then dilute with distilled water to a volume of about 1 l.

(e) Iodine Solution, 0.01 N. Dilute 25 ml. of the 0.1 N iodine solution to 250 ml. and standardize before use as follows. Take 25 ml. of the well-mixed iodine solution in a 250-ml. Erlenmeyer flask. Dilute to 100 ml. and add standard 0.01 N thiosulfate. As the end point is approached, add 10 ml. of 0.2% starch solution and titrate carefully until the solution is colorless.

(f) Iodine Solution, 0.001 N. Prepare by accurate dilution of freshly standardized 0.01 N iodine solution.

(g) Buffer Solution. Slowly add 20 g. of glacial acetic acid to a solution containing 80 g. of sodium carbonate and dilute to 1 l. with distilled water.

(h) Sodium Bisulfite, 1%. Dissolve 10 g. of sodium bisulfite in distilled water and dilute to 1 l.

Procedure

4. (a) To a 10-ml. portion of the scrubber solution in a 125-ml. Erlenmeyer flask add 0.1 N iodine solution until the end point is approached. Then add 10 ml. of starch solution and titrate until a dark blue color is obtained. Adjust the solution to a neutral point by decolorizing with 0.05 N sodium thiosulfate and bringing to a faint blue color with 0.01 N iodine.

(b) Chill the solution below 5°C in an ice bath and add 50 ml. of thoroughly chilled buffer solution. Titrate the liberated bisulfite with 0.005 N iodine. Take the end point as a blue color equal to the original faint color which holds for 45 seconds. Using 0, 0.1, 0.50, and 1.0 mg. samples of formaldehyde in 50 ml. of 1% sodium bisulfite solution, titrate in exactly the same manner as described in 4 (a) and (b) for the scrubber solution. Subtract the blank value (0 mg. of formaldehyde) and obtain the relation of standard iodine solution to formaldehyde.

Calculations

5. Calculate the aldehyde content of the solution as formaldehyde in the following equation:

$$\text{ppm Aldehyde as HCHO} = \frac{(A)(B)\,1000}{(W)}$$

where:

A = ml. of 0.005 N iodine consumed by sample,
B = mg. of formaldehyde titrated by 1 ml. of 0.005 N iodine, and
W = weight of original sample represented by aliquot taken in grams.

FORMALDEHYDE

Principle

Formaldehyde is absorbed in phenylhydrazine hydrochloride solution and a magenta colour is developed with potassium ferricyanide.

Apparatus

Plain bubbler, pump and flowmeter.

Spekker absorptiometer with 1 cm. cells and Ilford 604 filters.

Reagents

Phenylhydrazine reagent

Shake 1 g. phenylhydrazine with 5 ml. water, add 2 ml. concentrated hydrochloric acid and dilute to 80 ml. Filter and make up to 100 ml. with water.

Bisulphite reagent

Dissolve 10.40 g. sodium bisulphite in 1 liter water.

Standard formaldehyde solution

Determine the strength of a formalin solution (containing approximately 40 per cent formaldehyde) by the bisulphite method as follows: Dilute 10 ml. of formalin to 1 liter and place 25 ml. of this solution in a stoppered titrating flask. Add 50 ml. bisulphite solution and stand for 15 minutes. Determine excess bisulphite in the solution by titrating with 0.1 N iodine. Dilute this formalin solution to give a standard solution containing 7 micrograms formaldehyde per ml.

Potassium ferricyanide solution

Dissolve 5 g. A.R. potassium ferricyanide in 100 ml. water (prepare fresh as required).

Hydrochloric acid

A.R. hydrochloric acid.

Method

Dilute just before use 1 volume of phenylhydrazine reagent to 5 volumes with water and charge the bubbler with 10 ml. of the diluted solution. Sample for 5 minutes at 0.5 liter per minute.

Wash out the contents of the bubbler to 15 ml. with water and allow to stand for 10 minutes. Add 1 ml. potassium ferricyanide solution and 4 ml. hydrochloric acid. Stand for a further 10 minutes and make the colour measurement within the next 10 minutes using water as the reference liquid.

Calibration

Obtain a calibration curve by taking 0, 1.0, 2.0, 3.0, 4.0 and 5.0 ml. of standard formaldehyde solution, making up to 5 ml. with water, adding 10 ml. of diluted phenylhydrazine reagent and treating as above.

Typical calibration results are as follows:

micrograms formaldehyde	0.0	7.0	14.0	21.0	28.0	35.0
Spekker reading	0.01	0.26	0.59	0.87	1.15	1.43

Absorption Efficiency

One bubbler will absorb 95 per cent and two bubblers 99 per cent of the formaldehyde when sampling at 0.5 liter per minute. The maximum amount of formaldehyde which can be absorbed without the formation of a precipitate using the diluted phenylhydrazine reagent is about 0.05 mg.

Sensitivity and Specificity

Using the procedure recommended, the range covered is from 0.5 to 11 p.p.m. Higher concentrations may be estimated by using undiluted phenylhydrazine reagent as absorbent.

Ketones do not interfere; acetaldehyde and furfuraldehyde give distinguishable brown colours; acrolein gives a similar test to formaldehyde but of lower sensitivity.

References

The method is a modification of the procedure of Kersey, R.W., Maddocks, J.R., and Johnson, T.E. "The Determination of Small Amounts of Formaldehyde in Air", Analyst 65, 203 (1940).

TOTAL CARBONYL COMPOUNDS

Principle

Total carbonyl compounds are determined polarographically in an absorbing solution which is 0.1 molar in aqueous semicarbazide, sodium chloride, sodium acetate, and acetic acid.

Apparatus

Sargent Model XXI recording polarograph. An "H" type cell was used with provisions for flushing out the portion of the salt bridge adjacent to the dropping mercury electrode compartment.

Reagents

The scrubbing solution, which also serves as an aqueous supporting electrolyte solution, is 0.1 molar each in acetic acid, sodium acetate, sodium chloride, and semicarbazide.

Method

Total carbonyls in the air sample react with the absorbing solution to form semicarbazones, which are determined polarographically. As the polarographic sensitivity for various low weight aldehyde and ketone semicarbazones is essentially constant, the use of a single sensitivity factor is possible. This sensitivity factor "I" in the equation below gives the relationship between wave height at -1.4 volts vs S.C.E. and semicarbazone concentration.

$$C_s = \frac{i_d}{I m^{2/3} t^{1/6}}$$

C_s = millimolar semicarbazone concentration in aqueous solution

i_d = wave height or diffusion current in microamperes

I = diffusion current constant (or polarographic sensitivity factor)

m = rate of mercury flow through the polarographic capillary in mg/sec

t = mercury drop time in sec per drop

A typical polarogram is completed on the absorber solution.

Calibration

Known carbonyl-air mixtures are prepared by evaporating a small volume of a dilute benzene solution of a known carbonyl compound in the appropriate volume of air. The aldehyde - or ketone - air mixture is then drawn through the scrubber charged with semicarbazide solution. The concentration of semicarbazone in the scrubber solution is then determined polarographically.

Sensitivity and Specificity

The estimated precision of the analytical technique is ± 20% of the value if about 90% or more of the aldehydes and ketones are C_8 or lower.

References

Coulson, D. M., Polarographic Determination of Semicarbazones. Presented at XII International Congress of Pure and Applied Chemistry, Lisbon, Portugal, Sept. 10-12, 1956.

C. Acids as Acetic Acid

This component is analyzed by various methods by different investigators; in some cases the acidity to pH 7 is calculated as acetic acid while other investigators consider the titre from pH 2 to pH 7 as organic acids (calculated as acetic acid).

It is suggested that the 50-ml aliquot for analysis of acetic acid should be titrated potentiometrically with 0.05 N H_2SO_4. The acid titre from pH 2 to pH 7 is then calculated as organic acids as acetic acid.

Miller, et al. (9) describe the titration of acetic acid in water-glycerine with Fleisher's methyl purple indicator from a Kelley green color to purple.

No rapid method is available for the analysis of acetic acid.

D. Fluorides as Hydrofluoric Acid

Much research has been undertaken recently on analytical methods for fluorides. Stanford Research Institute methods for fluorides incorporates much if not all of the reported analytical improvements. For convenience, the ion exchange method described by Nielsen and Dangerfield (10) is more rapid than the distillation method. The ASTM has developed a proposed method for the determination of inorganic fluorides in the atmosphere.

It is expected that a portion of the gaseous hydrofluoric acid in the atmosphere will be adsorbed by the millipore holder and paper.

ASM 14.05
FLUORINE
PREPARATION
April 18, 1956

STANFORD RESEARCH INSTITUTE
ANALYTICAL SECTION METHOD

Preparation of

VARIOUS MATERIALS FOR FLUORINE ANALYSIS

Scope

1. This method is intended for the preparation of materials for analysis of fluorine. It is to be followed by ASM 15.05.

Outline of Method

2. Detailed procedures are given for the treatment of various materials such as vegetation, soils, ores, slags, dusts, coal and coke, particulate matter, and biological samples.

Reagents

3. (a) Sodium Carbonate, Technical Grade, if less than 1 ppm Fluorine.

(b) Phenolphthalein indicator. Dissolve 1 g. in 100 ml. of 95% ethyl alcohol.

(c) Sodium Hydroxide, Pellets. Baker of Mallinckrodt, C. P. grade.

(d) Calcium Chloride. $CaCl_2 \cdot 2H_2O$, C. P. Grade. Less than 20 ppm F.

(e) Calcium Hydroxide (low fluorine content). Dissolve 450 g. of calcium chloride dihydrate in 2000 ml. of distilled water contained in a 4000-ml beaker. Heat to 80° to 100°C and add 25 g. of sodium carbonate dissolved in 200 ml. of hot distilled water. Remove from the hot plate, stir occasionally, and let settle overnight. Filter through an 18-cm. No. 1 Whatman filter paper using a Buechner funnel and suction pump. Dissolve the precipitate adhering to the 4000-ml. beaker with a few ml. of dilute hydrochloric acid and discard. Return the filtrate to the 4000-ml. beaker. Discard the precipitate.

Heat the filtrate again to 80° to 100°C. Dissolve 350 g. of sodium carbonate in 1000 ml. of distilled water. Heat to effect solution. Add the sodium carbonate solution to the calcium chloride solution with stirring. Remove from the hot plate. Let stand 30 minutes, stirring occasionally, and again filter off the precipitate through an 18-cm. Buechner funnel using a suction pump. Discard the filtrate. Wash the precipitate eight or ten times with distilled water. Keep the precipitate wet enough when draining after each wash so that it does not crack. Transfer the precipitate to a large inconel dish. Dry on a hot plate or in an oven at 105°C. Transfer to a muffle furnace whose temperature does not exceed 300°C and raise the temperature gradually to 800°C. Continue heating at 800°C for 2 hours. Remove from the furnace and cool. Add water in small amounts until the CaO disintegrates or "slakes." Dry in an oven at 105°C overnight. Pulverize and transfer to a tightly stoppered bottle.

Note: A special low Fluoride grade calcium oxide may be purchased from Fisher Scientific Company.

Apparatus

4. (a) Metal Crucibles and Dishes, 125-, 200-, and 1000-ml. capacity. Nickel or. Inconel.

(b) Muffle Furnace, BKH Cat. No. 30730-31, Hevi-duty with rheostat and indicating pyrometer.

(c) Chipmunk Crusher, BKH No. 24134, U-belt drive with motor.

(d) Food Chopper, Hobart.

(e) Soxhlet Extraction Apparatus with suitable thimbles.

(f) Aspirating Pump.

(g) Urinometer, BKH No. 63282.

Procedure

5. (a) Blank. Determine a reagent blank with each string of samples.

(b) Vegetation.

(1) If the sample is too large for the analysis, obtain a representative aliquot by first putting it through the food chopper or otherwise reducing to small pieces. Mix thoroughly and remove one sample for moisture and a second sample for fluorine determination. (Note 1.) Weigh and record the weight of each sample. Place the moisture sample in a drying oven at 105°C and dry to a constant weight. Transfer the fluorine sample into a suitable nickel or inconel dish. Add 1 g. of calcium oxide for each 10 g. of green sample. Add sufficient

distilled water to cover the sample and mix well by stirring. Add a few drops of phenolphthalein indicator to test for alkalinity. Add more calcium oxide, if necessary, to maintain an alkaline condition during evaporation. Place on a hot plate and evaporate to dryness.

> Note 1. The size of the sample taken should be large enough to be representative of the material. An aliquot of 10 to 50 g. is usually satisfactory for a moisture sample and another aliquot of from 10 to 100 g. can be taken for the fluorine determination, depending on the concentration of fluorine in the materials. A reagent blank should be carried through the entire procedure with each string of samples.

Slowly introduce the dish containing the dry material into a muffle at a temperature of not more than 400°C so that the contents will not burst into flame. With the muffle open slowly raise the temperature to 600°C and continue heating until the ash is light grey in color. Stir the contents of the dish occasionally with a spatula if ignition is not complete after 1 hour. (Note 2.)

> Note 2. Both ignition time and temperature should be kept at a minimum or high and erratic blanks may result.

(2) After the ignition is completed, transfer the ash or an aliquot of it to a 200-ml. nickel or inconel dish. Add 5 to 10 g. of sodium hydroxide pellets. Place the dish in the muffle for 5 to 10 min at a temperature of 550 to 600°C. Swirl the contents of the crucible to facilitate mixing. Cool and add 50 ml. of distilled water. Cover the dish with a watch glass and heat to disintegrate the melt. Transfer to a distillation flask. Wash out the dist first with dilute distillation acid (25%) and finally with distilled water. (Note 3.) Add all the washings to the flask.

> Note 3. The volume in the flask including washings should not exceed 150 ml.

(c) Soils. Prepare a representative sample for analysis by drying the entire sample at room temperature, grinding with a mortar and pestle and screening through a 20-mesh screen. Grind the -20 mesh to a -80 mesh. (Note 4.) Roll well on a rubber sheet and cut the sample down to an appropriate size. Weigh 0.500 to 1.000 g. of a sample in a 200-ml. nickel or inconel dish and make the fusion as in the procedure for vegetation (b) (2).

> Note 4. The screening step is particularly important in the case of surface samples which usually contain roots and humus. Most of the organic matter is held back by the 20-mesh screen.

(d) Particulate Matter. Remove the filter paper containing the particulate matter from its holder. Roll up with the clean side out and place in a 200-ml nickel or inconel dish. Add 0.3 h. to 0.5 g. of calcium oxide. Wet with distilled water and take to dryness on a hot plate. Insert into a muffle without flaming and ash at 550 to 600°C for 1/2 hrs. Remove. Add 5 g. of sodium hydroxide pellets and fuse as in (b) (2).

(e) Water. Transfer a suitable portion of uniformly dispersed sample to a beaker. Make alkaline to phenolphthalein with sodium hydroxide and evaporate to a maximum volume of 125 ml. Transfer to a distilling flask and continue as in the procedure for distillation.

(f) Animal Tissue. Store the tissue in a frozen condition until ready for analysis. Reduce the material to small pieces, mix thoroughly and weight 25 g. to 50 g. into a 200-ml. nickel or inconel dish. Add 1 to 2 g. of calcium oxide. Cover with distilled water. Mix, evaporte to dryness, char slowly by placing in front of an open muffle, and finally heat at 550 to 600°C until a white or grey ash remains. Remove from the muffle, transfer the ash to a distillation flask. Wash crucible with dilute perchloric acid. Transfer the acid to the flask and wash the crucible twice with distilled water, transferring the washings to the flask.

(g) Blood. Add the required volume of anti-coagulant to a 250-ml. flask marked at the 200 ml. level and tare. Shake the flask vigorously while enough blood is added to reach the 200 ml. mark. Stopper the flask with a cotton plug and continue shaking for four minutes. (Note 5.) Reweigh the flask and obtain the weight of the blood by difference. Store the sample at 32 to 40°F until ready for use.

> Note 5. A suitable anti-coagulant is a 2% solution of potassium oxalate which should be added in a concentration of 0.1 ml. per ml. of blood.

Transfer a 25 ml. aliquot to suitable nickel or inconel crucible and add 1 g. of calcium oxide. Cautiously evaporate to dryness, without foaming. Maintain an alkaline condition during evaporation by adding more calcium oxide, if necessary. Place the dish in a muffle at 550 to 600°C until a white or grey ash remains. Transfer the dry ash to a distilling flask. Cover the dish and dissolve the remaining ash in dilute perchloric acid. Transfer the acid and subsequent washings to the flask.

(h) Coal and Coke. Weigh 5 g. of sample into a 200-ml. nickel or inconel crucible. Add 0.1 g. of calcium oxide wet with water and evaporate to dryness on a hot plate. Insert into a muffle, without flaming, and ignite at a temperature of 550 to 600°C until a white or grey ash remains. Cool and add 5 g. of sodium hydroxide pellets and continue as in (b) (2).

(i) Urine. If urine is to be transported or stored, first take the specific gravity by means of a Urinometer, then add 1 ml. of chloroform. Pipette 25 to 50 ml. of sample into a 200 ml. inconel dish. Add 0.5 g. of CaO, stir, and evaporate to dryness on a hot plate. (CAUTION: spitting may occur if plate is too hot.) Ignite in a muffle using same procedure as for vegetation -- (b) (1). Omit the fusion with sodium hydroxide. Transfer the ash directly to a distilling flask.

(j) Bones. Trim the bones of all the meat and tissue possible. Saw them longitudinally and place in an oven at 105°C for 2 hours or more. This removes most of the fats and oils. Put each sample through a chipmunk crusher until the bone is crushed to the size of 1/8 in. or less. (Note 7.) (This usually requires about three passes through the crusher when it is set with the opening at its minimum width.) Place about 20 g. of sample in a Soxhlet thimble and extract with ether for four hours. (Note 6.) Transfer the extracted sample to a beaker and dry for 1 hr. in air and 15 min. in an oven at 105°C. Cool in a desiccator and weight 10 g. into a 125-ml. nickel crucible. Add 0.25 g. of calcium oxide wet with water and evaporate to dryness on a hot plate. Ash the sample using the same procedure as for ashing vegetation. When the ashing is completed (this usually takes 1 to 2 hours) cool in a desiccator and weigh the ash. Pulverize with a mortar and pestle and transfer to a stoppered bottle. Weigh 0.5 to 1 g. directly into a distilling flask.

Note 6. Extraction of the fats by digestion with ether may be substituted for the refluxing procedure. Place 20 g. of sample in a stoppered bottle and add 75 ml. of ether. Let stand 2 hours with occasional shaking then decant off the ether. Make at least four extractions with successive portions of ether.

Note 7. An excellent alternate method is to drill the bone with a 1/4-in. drill using a drill press, covering the entire section of the bone with a uniform pattern of holes.

ASM 15.05
FLUORINE TITRATION
April 18, 1956

STANFORD RESEARCH INSTITUTE
ANALYTICAL SECTION METHOD

Determination of

FLUORINE
DISTILLATION AND TITRATION

Scope

1. This method is intended for the determination of fluorine in solutions or suspensions after a suitable preparation of the sample.

Outline of Method

2. The fluorine is separated by a single distillation with perchloric acid at 135°C using the conventional Willard and Winter method. After collecting sufficient distillate to insure complete separation, the fluorine is determined by a direct titration with thorium nitrate using sodium alizarin sulfonate as an indicator.

Reagents

3. (a) Silver Sulfate, C.P. Crystals

(b) Perchloric Acid (70-72%)

(c) Thorium Nitrate, 0.1 N. Dissolve 13.805 g. of hydrated thorium nitrate ($Th(NO_3)_4.4H_2O$) in water and make up to 1 liter. Dilute to 1/10 this concentration for 0.01 N solution.

(d) Sodium Fluoride Solution, 1 mg. F per ml. Dry C.P. sodium fluoride at 105°C to a constant weight. Cool in a desiccator. Dissolve 2.210 g. in distilled water and make up to 1 liter.

(e) Sodium Fluoride Solution, 0.01 mg. F per ml. Dilute 10 ml. of solution (d) to 1 liter.

(f) Sodium Alizarin Sulfonate, Aqueous, 0.05%.

(g) Sodium Hydroxide Solution, 0.05 N. Dissolve 2 g. of sodium hydroxide in 1 liter of distilled water.

(h) Hydrochloric Acid, 0.05 N.

(i) Buffer Solution. Dissolve 2.0 g. of sodium hydroxide in 40 ml. of distilled water. Dissolve 9.5 g. of monochloroacetic acid in 60 ml. of distilled water. Slowly add the sodium hydroxide solution, with stirring, to the monochloroacetic acid solution. This solution is stable for five days.

Apparatus

4. (a) Steam Generator

(1) Erlenmeyer Flask, BKH No. 29136, 6000 ml. capacity.

(2) Rubber Stopper No. 6, 2-hole.

(3) Heater, electric BKH No. 33985, 2000 watts, 115 volts, 8-1/2-in. diameter.

(b) Distillation Apparatus

(1) Distillation Flasks, Claissen, BKH No. 29250, 250 ml. capacity (bottoms flattened to fit electric plate).

(2) Electric Heater, BKH No. 33825, 550 watts, 115 volts.

(3) Condenser, West, BKH No. 23133, length of jacket, 300 mm.

(4) Flasks, Volumetric, BKH No. 29621X, 250 ml. and 500 ml. capacity, glass-stoppered.

(c) Flasks, Titration. BKH No. 29140, Wide Mouth, 250 ml. capacity.

(d) Burets (4). BKH No. 17455, 25 ml. capacity

(e) Buret (1), Koch, BKH No. 17478, with two way stopcock. Capacity 5 ml. Subdivisions, 1/100 ml.

(f) Pipettes, Normax, BKH No. 53047. One each of a 5, 10, 25, 50 ml. capacity.

(g) Thermometers, Yellow Back, Central Scientific Company, Chicago, Illinois, Cat. No. 19242-C, Range -5 to 200°C.

(h) Rubber Stoppers No. 3, one-hole and two-hole.

(i) Glass Tubing, 6 mm O.D.

(j) Glass Beads, 4 mm. diameter.

(k) Distillation Rack, constructed to support sixteen distilling units. The steam is conducted by rubber tubing from a steam manifold to a glass capillary tube 3/4 in. long and with a capillary of 1.25 mm diameter. The capillary is connected to the glass tube entering the distilling flask by means of rubber tubing. A pinch clamp is fitted over this rubber tubing and is used to turn the steam on during the distilling operation. The distilling flask is fitted with a 2-hole stopper through which is inserted a thermometer and the steam tube. The thermometer and the steam tube extend to within 1/8-in. of the bottom of the distilling flask.

Procedure

5. (a) Add 0.1 g. of calcium hydroxide to each steam still. Add distilled water to the still unless the regular tap water is known to be acceptable. Add a few glass beads or brick chips to prevent bumping and insure smooth boiling. (Note 1.Note 2)

> Note 1. Two of the preceding stills will generate sufficient steam for the distillation of sixteen samples in a period of three to three and one-half hours. A "wet" steam or a steam contining some water is more efficient in volatilizing fluorine from the solution in the distilling flask than a "dry" steam.

> Note 2. If regular distilled water titrates the same as water from the fluorine stills, it may be used in diluting standards and aliquots and for a titration blank. Otherwise water distilled from the fluorine stills must be used for these purposes.

(b) Transfer the sample after suitable preparation to a clean Claissen distilling flask. (Note 3.) Add 8 or 10 glass beads and sufficient silver sulfate to precipitate all the chlorides present in the solution of the sample. Add 50 ml. of perchloric acid. Add distilled water, if necessary, to make the volume of solution in the flask about 175 ml. Wash down the neck of the flask and connect to the condenser. Insert the two-hold stopper containing the steam tube and thermometer into the neck of the flask. Connect the steam tube to the capillary valve with a minimum of rubber tubing. Close the rubber tube with the pinch clamp and heat the distilling flask to boiling. Collect the distillate through the water-cooled condensers into 250-ml. or 500-ml. volumetric flasks. (Note 4.) When the temperature in the flask reaches 132°C, reduce the current input of the electric heater by means of the rheostat and open the pinch clamp to allow the steam to enter the flask. Collect sufficient distillate to completely distill all the fluorine in the distillation flask.

> Note 3. Flasks should be well scrubbed with soap, brush and hot water after each distillation. If much silver chloride is present, a rinse with dilute ammonium hydroxide

will aid in removing it. If silica is adhering to the inside of the flasks, boiling in 10% sodium hydroxide will usually remove it. The final washing should be with hot water followed by rinsing with distilled water in any case. Flasks previously used for samples containing high fluoride concentrations should not be used again unless special precautions are used in cleaning the flasks. The same limitations apply in the use of dishes or crucibles used in ashing and fusing samples. Stiff brushes and abrasive cleaners help in removing scale from the metal dishes and crucibles.

Note 4. Most samples will require 500 ml. of distillate to recover all the fluorine in the flask. If substances which retard the volatilization of fluorine, such as aluminum or silica, are present in appreciable quantities, it may be necessary to collect 750 ml. when such substances are known to be present or if the fluorine content is known to be high. The smaller the sample used the more complete the recovery will be using the same procedure. With significant amounts of aluminum present (50 mg. or more) low results will be obtained with distillation at 135°C. The distillation should be made using sulfuric acid and a temperature of 150°C.

(c) Direct Titration. Standardize the approximately 0.01 normal thorium nitrate solution as follows: Pipette samples of standard sodium fluoride solution directly into titrating flasks. Use concentrations of 10 to 300 μg of fluorine. Make up to 200 ml. volume with water collected from the fluorine stills or its equivalent. Add 1 ml. of 0.05% alizarin red indicator and restore the pink color by adding 0.05 normal sodium hydroxide solution drop by drop. Just discharge the pink color by dropwise addition of 0.05 normal hydrochloric acid. Add 1 ml of monochloroacetic acid buffer solution and titrate with 0.01 normal thorium nitrate solution to the appearance of a faint pink color. (Note 5.)

Note 5. The blank is first titrated with 0.13 to 0.16 ml of thorium nitrate solution after the addition of the other reagents and all the subsequent samples are compared to this blank.

Subtract the volume of thorium nitrate used on the blank from the volume used on each standard. Construct a table to relate the quantity of fluoride taken to the volume of thorium nitrate used. (Note 6.)

Note 6. Standards should also be subjected to the same procedure as the samples and checked against similar concentrations titrated directly.

Take a suitable aliquot of the distillate from each sample and dilute to 200 ml. if necessary, with distilled water from the stills or its equivalent. Add indicator, sodium hydroxide, hydrochloric acid, and buffer solutions in the same manner as described for the standardization of the thorium nitrate solution. Titrate an aliquot of the sample to the color produced in the titration blank. Titrate a similar aliquot of the reagent blank and subtract the milliliters of thorium nitrate solution used by the reagent blank from the milliliters used by the sample. From the above table determine the micrograms of fluorine found in the aliquot of the sample.

Calculations

6. The parts per million of fluorine in the sample are calculated as follows:

(a) ppm fluorine, dry weight bases $= \frac{A \times B}{C \times D}$

where:

A = micrograms of fluorine found in the aliquot titrated,
B = total volume of the distillate,
C = dry weight of the sample
D = volume of the aliquot.

(b) Samples of urine

ppm fluorine, "as received" basis $= \frac{A \times B}{C \times D \times E}$

where:

A = micrograms of fluorine found in the aliquot titrated,
B = total volume of the distillate
C = ml. of sample used,
D = volume of aliquot used,
E = specific gravity of the urine.

ppm fluorine at specific gravity of 1.030 $= \frac{A \times 0.030}{E - 1.000}$

where:

A = ppm F "as received"
E = specific gravity of the urine.

E. Carbon Dioxide

Methods for the analysis of carbon dioxide have been based upon evolution of the gas from an acidified solution either by weighing or titrating the evolved carbon dioxide. The bleaching of phenophthalein color has also been used for the determination of carbon dioxide.

Spector and Dodge (11) have described a colorimetric method for determination of traces of carbon dioxide.

ASM 1.01
CARBON DIOXIDE
INORGANIC
March 9, 1950

STANFORD RESEARCH INSTITUTE
ANALYTICAL SECTION METHOD

Determination of

CARBON DIOXIDE IN INORGANIC MATERIALS
EVOLUTION METHOD

Scope

1. This method is intended for the determination of carbon dioxide in inorganic materials such as clays, rocks, sands, etc. It is, indirectly, a measure of the carbonate in the material.

Method Summary

2. A finely divided sample is added to a weighed amount of dilute hydrochloric acid contained in evolution apparatus. The apparatus is weighed before and after the carbon dioxide is evolved and loss in weight is calculated as carbon dioxide.

Reagents

3. (a) Hydrochloric Acid, 6 N.

(b) Dehydrite

Apparatus

4. Evolution Apparatus, fitted with an entrance tube to permit a flow of air to liquid in the bottom of the flask, and a Dehydrite tube to absorb any water carried out with the evolved carbon dioxide.

Procedure

5. (a) Add 10 ml. of 6 N hydrochloric acid to the flask of the evolution apparatus. Weigh a 1 g. portion of a finely divided sample in a glass cup and carefully place it in the apparatus. Immediately close the apparatus by inserting the stopper containing the entrance tube and and the dehydrite tube, (Note 1).

Note 1. The entrance and exit tubes must be closed to prevent loss of carbon dioxide. A rubber policeman on each is satisfactory.

(b) Weigh the apparatus on an analytical balance, remove the closure from the dehydrite tube, and shake the apparatus to permit thorough contact of the acid with the sample. After cessation of bubbles, attach an air line to the entrance tube and purge with air for five min. Replace the closures on the tubes and reweigh.

Calculation

6. Calculate the carbon dioxide in the sample by means of the following equation:

$$\text{Carbon dioxide, \% w} = \frac{(A - B)}{W} 100$$

where:

A = weight of apparatus plus sample before evolution, in grams
B = final weight of apparatus, in grams, and
W = weight of sample, in grams.

STANFORD RESEARCH INSTITUTE
PASADENA LABORATORY

Determination of

CARBON DIOXIDE
COLORIMETRIC METHOD

Scope

1. This method is adaptable to the determination of CO_2 in concentrations above 10 ppm by volume, in the absence of other acidic gases. It is particularly useful for determinations in the range of 10 to 300 ppm of CO_2 in the air.

Outline of Method

2. Carbon dioxide is absorbed in dilute caustic solutions tinted with phenolphthalein by shaking of a known volume of air with the caustic solution in a separatory funnel. The bleaching of the pink phenolphthalein color is determined colorimetrically and is a measure of the amount of CO_2 present.

Reagents

3. (a) Sodium hydroxide, 0.0002 n. Dilute 2 ml. 0.1 N NaOH to 1,000 ml. with distilled water. The normality of this reagent does not have to be accurately known.

(b) Phenolphthalein indicator solution.

Apparatus

4. (a) Calibrated separatory funnel. A 1,000 ml. (nominal) separatory funnel is calibrated by marking the first 50 ml. and determining its total volume. A so-called French-type globe funnel (which looks somewhat like an inverted volumetric flask) is preferable, but has to be made to order in the 1,000 ml. size; a pear-shaped funnel is satisfactory.

(b) The colorimeter. A Lumetron colorimeter, Model 402-E, equipped with Corning filters Nos. 3384, 4303, and 5031 (peaked at 515 mμ), and a 100 mm. cell, was used in this laboratory. Any other filter colorimeter or spectrophotometer could be used, provided it accomodates a 100 mm. cell.

Procedure for the Determination of CO_2 Concentrations of the order of 10 to 100 ppm by volume

5. (a) Preparation and storage of tinted caustic solutions. The approximately 0.0002 N NaOH solution is tinted by the addition of a sufficient amount of phenolphthalein indicator solution to give a transmission of 10-20% when placed in the colorimeter, using a 100 mm. cell. This requires about 1.2 ml. indicator solution per liter of 0.0002 N caustic.

The tinted solution is reasonably stable if stored in a polyethylene bottle protected by a soda lime tube.

(b) Calibration of tinted NaOH solution. The separatory funnel is rinsed with a small amount of caustic solution, which is discarded, then filled completely with absorbing solution. If this is done quickly, no discoloration of the solution will be noticed. The top of the separatory funnel is then connected to the source of the known CO_2 sample*, and the gas sample admitted by draining the absorbing solution to the 50 ml. mark. Approximately 1000 ml. of gas sample is thus introduced, the exact amount having been determined previously. No bleaching of the reagent occurs during this period. The sample is then shaken for 5 min. with the absorbing solution, the latter transferred into the optical cell (which should be purged with nitrogen for accurate results) and its transmission determined.

(c) Sampling procedure. Actual samples are introduced, reacted and measured exactly as described above. The CO_2 concentration can then be read off the calibration graph. If higher concentrations of CO_2 are present, a different proportion of gas to liquid may be used. It is advisable to secure a new calibration curve under these conditions, rather than relying on extrapolations of the original curve.

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* A polyethylene bag of about 10 cu. ft. volume is useful for the preparation of the known samples of CO_2 in nitrogen.

F. Sulfur Dioxide

Sulfur dioxide is absorbed in sodium hydroxide, using glycerine to repress the oxidation to sulfate. The resulting solution may be analyzed gravimetrically, polarographically, iodometrically, or colorimetrically.

The Mine Safety Appliance Company (12) gel indicator for sulfur dioxide may be used as a rapid method of analysis. Pearce and Schrenk (13) determined air concentrations with the midget impinger.

ASM 8.01
SULFUR DIOXIDE
GRAVIMETRIC
May 1, 1950

STANFORD RESEARCH INSTITUTE
ANALYTICAL SECTION METHOD

Determination of

SULFUR DIOXIDE IN ABSORBER SOLUTIONS GRAVIMETRIC PRECIPITATION METHOD

Scope

1. This method is intended for the determination of sulfur dioxide in sodium hydroxide absorber solutions. Correction is made for any sulfur trioxide which is absorbed in the alkaline medium.

Outline of Method

2. Aliquots of the sodium hydroxide absorber solution are taken for analysis. Total sulfur is determined on one aliquot by precipitation as barium sulfate after oxidation with bromine. To correct for sulfur trioxide a second aliquot is acidified and boiled to expel sulfur dioxide before precipitation of barium sulfate.

Reagents

3. (a) Barium Chloride Solution. Prepare by dissolving 100 g. of c.p. barium chloride dehydrate in 1 liter of distilled water.

(b) Bromine Water, Saturated. To 200 ml. of distilled water in a glass-stoppered bottle add 10 ml. of c.p. bromine and shake to saturate.

(c) Wash Solution. Saturate 1:300 hydrochloric acid with barium sulfate.

(d) Hydrochloric Acid, 6 N.

Procedure

4. (a) Adjust the volume of the absorber solution to 100 ml. in a volumetric flask. Pipette 25 ml. aliquots into separate 125-ml. beakers.

(b) Boil one of the aliquots for 10 minutes to remove benzyl alcohol. Add 1 or 2 ml. of saturated bromine water and add hydrochloric acid dropwise until the solution is just acid to methyl orange. Evaporate nearly to dryness under an air stream to expel excess bromine. (Note 1.)

Filter if necessary to remove foreign materials and adjust the volume to 40-50 ml. Add 2 ml. of 6 N. HCl and heat to boiling. Add from a pipette 10 ml. of barium chloride solution dropwise or in a fine stream. Stir constantly during the addition and for 2 minutes afterwards. Allow the mixture to settle by digesting at 75 ±15°C for 1 hour on a hot plate and allowing to stand an additional hour while cooling. Filter the supernatant liquor through a close texture filter paper (e.g. Whatman No. 44). Wash the precipitate with the wash solution first by decantation and then on the filter paper until free from chloride ion.

(c) Transfer the paper and precipitate to a previously ignited and weighed porcelain or platinum crucible and dry in an oven at 110°C. Char the paper completely over a burner without igniting it, ignite at 500 to 550°C in a muffle furnace until all the paper is burned off, and finally heat at 750 to 800°C for 30 min. Cool the crucible to room temperature in a desiccator jar without drying agent and weigh.

(d) To the other aliquot add hydrochloric acid to neutralize to methyl orange and then add 5 ml. in excess. Boil for 15-20 minutes to expel benzyl alcohol and sulfur dioxide. Filter if necessary to remove foreign material and adjust the volume to 40 or 50 ml. Heat to boiling and add 10 ml. of barium chloride solution dropwise in a fine stream. Stir, digest, filter, and wash as described in 4 (b).

(Note 2.) (e) Treat the paper and precipitate as described in (c) above.

Note 1. Do not evaporate completely to dryness as spattering may occur.

Note 2. This weight represents sulfur other than that in sulfur dioxide and is used to correct the value for sulfur dioxide found in (c). It is also used as a positive correction in the determination of sulfur trioxide described in a separate method (ASM 9.01).

Calculations

5. Calculate the sulfur dioxide content of the sample by means of the following equation:

$$\text{Sulfur dioxide, ppm} = \frac{(A-B)\ (0.2746)\ (1000)}{(W)}$$

where:

A = weight of barium sulfate in mg. in total sample found after bromine oxidation
B = weight of barium sulfate in mg. in total sample found after expelling sulfur dioxide, and
W = weight of original sample in grams represented by the aliquot taken.

SULFUR DIOXIDE

Principle

Sulfur dioxide is absorbed in sodium hydroxide solution containing glycerine to inhibit the oxidation to sulfate. The sulfur dioxide present is determined polarographically.

Apparatus

Sargent Model XXI Visible Recording Polarograph with special dearation chamber (see reference).

Reagents

Acetate Buffer, 2.5 M acetic acid in 0.5 M sodium acetate. This gives a pH of 3.85-3.95.

Standard Sulfite Solution, Sodium metabisulfite was added to the collection medium (0.05 N sodium hydroxide plus 2% glycerine) to give the equivalent of 100 μg SO_2/ml. Solution standardized with 0.01 N iodine solution.

Standardization

Each of a series of standard solutions containing from 0 to 10 μg SO_2/ml was run by placing a measured amount of the solution (5 to 20 ml) in the electrolysis vessel, and an equal amount of acetate buffer in the deaeration chamber. Oxygen was removed by bubbling nitrogen through these two solutions in series by means of the deaeration chamber. Combine both solutions in electrolysis vessel. Polarogram was made from -0.35 to -1 volts. A sensitivity of 0.006 microamperes/min was normally used. Standard curve was constructed from the diffusion currents indicated by these polarograms for several concentrations of SO_2.

Analysis

The analysis of the test sample is completed as described above. As some sulfur dioxide is lost in the removal of oxygen, an arbitrary stirring time was used. The stirring time of 1-1/2 minutes was chosen, timed from the opening of the stopcock of the deaeration chamber for the release of the buffer solution into the sample.

Sensitivity

Concentrations as low as 0.5 μg SO_2/ml of sample were determined with an accuracy of ±10%. The standard curve (concentration vs. wave height) was a straight line which passed through the zero point. Reproducibility ±2%. Results by this method were consistently low, compared to the fuchsin method, by 2 to 7%:

Reference: Paulus, H. J., E. P. Floyd, and D. H. Byers. Determination of sulfur dioxide in atmosphere samples. Ind. Hyg. Assoc., Q. 15(4), 277-282 (1954)

SULFUR DIOXIDE

Principle

Sulfur dioxide is absorbed in sodium hydroxide solution containing glycerine to inhibit the oxidation to sulphate. The resulting solution is analysed by titration with standard iodine solutions.

Apparatus

Bead bubbler, pump, and flowmeter.

Reagents

Iodine solution 0.02 N, Dissolve 1.2 g of iodine in 20 ml water containing 10 g potassium iodide and then dilute to 500 ml. Standardize against arsenious acid.

Arsenious Acid 0.05 N, Weigh accurately about 1.25 g arsenious oxide and dissolve in 10 ml 2 N sodium hydroxide solution with warming. Make solution and washings acid to phenolphthalein with dilute hydrochloric acid and dilute to 500 ml with water.

Sodium thiosulphate 0.02 N, Dissolve 2.182 g of A.R. sodium thiosulphate and 0.1 g sodium carbonate in water, make up to 500 ml and standardize against 0.02 N iodine solution.

Starch Solution, Mix 1 g soluble starch to a paste with water and pour, with stirring, into 200 ml boiling water. (Prepare a fresh solution each day.)

Absorbing Solution, Dissolve 5 g sodium hydroxide and 0.1 g glycerine in 100 ml water.

Sulfuric Acid, Dilute 100 ml. A.R. sulfuric acid (S.G. 1.84) to 1 liter.

Method

Charge the bubbler with 15 ml absorbing solution and sample at 10 liters per minute for 1 hour.

Wash the contents of the bubbler into a titrating flask, acidify with sulfuric acid and titrate with iodine, using starch solution as indicator (Note 1). Carry out "blank" determinations.

Note 1. If the temperature is high or large amounts of sulfur dioxide are expected, it is preferable to add excess iodine and titrate the excess with sodium thiosulphate solution.

Calculation

1 ml of 0.02 N iodine is equivalent to 0.6406 mg sulfur dioxide.

Absorption Efficiency

One bubbler will absorb approximately 90 percent and two bubblers 99 percent of the sulfur dioxide when sampling at 10 liters per minute.

Sensitivity and Specificity

Using the procedure recommended 0.1 ml of 0.02 N iodine corresponds to 0.04 ppm of sulfur dioxide.

Other substances oxidisable by iodine will interfere.

Reference: The use of glycerol as an inhibitor in the absorbent has been described by Gillam, E. W. C., Determination of oxides of sulphur in flue gas. J. Soc. Chem. Ind. 65, 370 (1946)

SULFUR DIOXIDE

Principle

Sulfur dioxide is absorbed in sodium hydroxide solution containing glycerine to inhibit the oxidation to sulfate. The sulfur dioxide present is determined with a basic fuchsin-formaldehyde color reagent.

Apparatus

Beckman Model DU Spectrophotometer, 20 mm cell.

Reagents

Stock Solution I. Shake a mixture of 460 ml water, 44 ml concentrated sulfuric acid and 16 ml of a 3% solution of basic fuchsin in ethyl alcohol. Add 280 ml water and 4 g of Norite A activated carbon; shake and refrigerate overnight. Filter to remove carbon. If the stock solution is refrigerated, it will remain stable for several months.

Stock Solution II. Dilute 5 ml of 40% formaldehyde with water to 100 ml.

Color Reagent. One part of solution II was added to 10 parts of solution I, mixed, shaken, and used after 30 minutes.

Standard Sulfite Solution. Sodium metabisulfite was added to the collection medium to give the equivalent of 100 μg SO_2/ml. Solution standardized with 0.01 N iodine solution.

Standardization

A series of solutions were prepared containing from 1 to 10 μg of SO_2/ml of medium (0.05 N NaOH and 2% glycerine). One ml of each standard solution placed in 20 mm transmission cell along with 10 ml of collecting medium and 5 ml of color reagent. Color was read at 570 mμ with a slit width of 0.03 mm after 10 to 20 minutes.

Analysis

Air samples were treated in a similar manner except that the amount of test solution added to the transmission cell depended upon the sulfur dioxide concentration. The total volume of test solution and any additional collection medium should equal 11 ml; 5 ml of color reagent is always added.

Sensitivity

Minimum detectable quantity if 0.1 μg/ml. Greatest accurcy at 2 to 10 μg/ml. Reproducibility ±2%:

Reference: Paulus, H. J., E. P. Floyd, and D. H. Byers. Determination of sulfur dioxide in atmosphere samples. Ind. Hyg. Assoc., Q. 15(4), 277-282 (1954)

G. Oxides of Nitrogen

The absorbed nitrogen dioxide in the caustic scrubber may be analyzed by either the phenoldisulfonic acid method or the Saltzman reagent.

The Mine Safety Appliances Company (14) has a gel indicator for nitrogen dioxide. Other workers (15,16) have also described such gels for nitrogen dioxide.

ASM 202.01
NITROGEN OXIDE
COLORIMETRIC
May 1, 1950

STANFORD RESEARCH INSTITUTE
ANALYTICAL SECTION METHOD

Determination of

NITROGEN OXIDES
PHENOL DISULFONIC ACID METHODS

Scope

1. This method is intended for the determination of oxides of nitrogen on an absorption sampling train or a sampling bottle. The method is applicable to the determination of nitrous oxide (NO) and nitrogen dioxide (NO_2), but tends to give high values for nitrogen dioxide.

Method Summary

2. The color developed by nitrate when treated with phenol disulfonic acid solution is used as a measure of the NO_2 in the alkaline sample solution and as a measure of total oxides of nitrogen after a preliminary treatment with hydrogen peroxide. The color is developed after making strongly acid and boiling, then neutralizing and evaporating to dryness. Transmission measurements are made using a spectrophotometer or a colorimeter at a wave length of 410 mμ, and compared with a standard prepared in a similar manner with known concentrations of nitrate.

Reagents

3. (a) Phenol Disulfonic Acid Solution. Dissolve 25 g of pure white phenol in 150 ml of concentrated sulfuric acid. Add 75 cc of fuming sulfuric acid (13-15% SO_3) and heat at 100°C for 2 hours.

(b) Hydrogen Peroxide, 3% Solution. Obtain a 30% hydrogen peroxide reagent which is low in nitrogen and dilute 10 ml to 100 ml with distilled water.

(c) Potassium Hydroxide, 5%. Dissolve 5 g of reagent grade potassium hydroxide in 100 ml of water.

Apparatus

4. (a) Beckman Spectrophotometer, Model DU, equipped with 1-cm cells is suitable. A good colorimeter, such as a Lumetron Model 42A, having a narrow filter in the range of 410 mμ can be substituted.

(b) pH Test Paper. This paper or series of papers should be capable of indicating the pH in the range of fairly high acidity and in the neutral range such as "pHydrion papers" A or B.

Procedure for Total Oxides of Nitrogen

5. (a) Dilute the individual solutions to convenient volumes. Combine 5-ml aliquots of each of the potassium hydroxide solutions in a small beaker. Add 1 ml of 3% hydrogen peroxide and acidify to a pH of about 1, using 1-ml portions of 1 N sulfuric acid. Heat to boiling on a hot plate and add 5% potassium hydroxide in small portions, checking with test paper until the pH is 8 or higher. Evaporate just to dryness, taking care to avoid loss by spattering. (Note 1). Then remove from the hot plate. Add 1 ml of phenol disulfonic acid reagent, measured with a rapid-flowing pipette and stir rapidly with a stirring rod to insure intimate contact and minimize loss due to carbonates. Add 4 ml of water and mix to dissolve the salts. Place the beaker in a cooling tray and add ammonium hydroxide in small portions until an excess is indicated by color and checked by the odor. Transfer to a graduated 10-ml test tube, dilute to the mark and mix. Filter through a dry medium filter paper into dry absorption tubes and read the transmission at 410 mμ. From a previously prepared calibration curve obtain the mg of nitrate as NO_2 in the sample. Carry a blank through with each series of samples, making appropriate corrections.

Note 1. The acidification after addition of hydrogen peroxide is necessary to obtain complete oxidation of nitrite. The subsequent neutralization before evaporating to dryness is to prevent loss and to prevent formation of a brown color.

(b) Combine 5-ml aliquots of potassium hydroxide-peroxide solutions and sulfuric acid-peroxide solutions which have been diluted to a convenient volume and treated as above. Analyze a blank using an equivalent amount of the same solutions as used in sampling. (Note 2).

Note 2. Hydrogen peroxide normally contains an appreciable quantity of nitrate ion.

Procedure for Nitrate

6. Combine 5-ml aliquots of the potassium hydroxide absorber solutions and add 1 ml of 1% sodium bisulfite. (Note 3). Add 5 ml of 1 N sulfuric acid and additional portions as necessary to obtain a pH of 1. Heat to boiling for 5 minutes and add small portions of 5% potassium

hydroxide until pH 8 is reached. Evaporate to dryness using care to avoid spattering and continue as directed in Paragraph 5 (a) above. Subtract an appropriate blank.

> Note 3. Sodium bisulfite is added to minimize oxidation of nitrite to nitrate. The acidification and heating is to remove any nitrite and to prevent formation of a green color upon addition of phenol disulfonic acid.

Calculations

7. (a) Calculate the total oxides of nitrogen present in the absorber solution in mg:

Total oxides of nitrogen as NO_2, mg = A + B

where

A = mg of NO_2 found in Paragraph 5 (a), and
B = mg of NO_2 found in Paragraph 5 (b).

(b) Calculate the nitrate ion from the absorber solutions as follows:

Nitrate ion as NO_2, mg= (C)(D)(2)

where

C = mg of NO_2 found in Paragraph 6, and
D = dilution factor.
2 = factor of nitrate to NO_2, assuming that the over-all reaction taking place during sampling is:

$$2NO_2 + 2KOH \longrightarrow KNO_2 + KNO_3 + H_2O$$

NITROGEN DIOXIDE

Principle

Nitrogen dioxide is absorbed in a mixture of sulfanilic acid, N-(1-naphthyl)-ethylenediamine dihyrochloride, and acetic acid. Efficiency of midget fritted bubblers is good.

Apparatus

Beckman Model DU Spectrophotometer and matched test tubes 22x175 mm.

Midget fritted bubblers of 60 ml capacity, with upward-facing, 8-mm diameter fritted discs. Using 10 ml of absorbing reagent, the air sampling rate is 0.4 liters/min.

Reagents

N-(1-Naphthyl)-ethylenediamine Dihydrochloride, 0.1%. Dissolve 0.1 g of reagent in 100 ml water. Stock solution.

Absorbing Reagent. Dissolve 5 g of sulfanilic acid in almost a liter of water containing 140 ml of glacial acetic acid, add 20 ml of the 0.1% stock solution of N-(1-naphtyl)-ethylenediamine dihydrochloride and dilute to 1 liter.

Standard Sodium Nitrite Solution. 0.0203 g/liter. One ml of this working solution produces a color equivalent to that of 10 μl of nitrogen dioxide (10 ppm in 1 liter air). Prepare fresh by dilution from a stronger stock solution. A stock solution of 8 g/liter was found to be stable for 90 days.

Standardization

Add graduated amounts of standard sodium nitrite solution up to 1 ml to a series of 25 ml volumetric flasks, and dilute to mark with absorbing reagent. Mix, allow 15 minutes for complete color development and read color in a spectrophotometer at 550 mμ, using unexposed reagent as a reference. The 1 ml standard is equivalent to 4 μl of nitrogen dioxide per 10 ml of absorbing solution.

Analysis

After collection or absorption of the atmosphere sample, a direct red-violet color appears. Color development is complete within 15 minutes at ordinary temperatures. Read colors in spectrophotometer 3-4% loss in absorbence per day. Results by this method were systematically high compared with the phenoldisulfonic acid procedure. The effect of various interfering gases was found to be unimportant unless the concentration was much higher than that of the nitrogen dioxide. Ozone in a five-fold excess does interfere but this compound can be destroyed at room temperature by passage over specially prepared manganese dioxide catalyst.

Sulfur dioxide, nitric acid, formaldehyde, and hydrogen sulfide do not interfere. Chlorine and hydrogen peroxide partially interfere at a 10-fold excess.

Sensitivity

Sensitivity of a few parts per billion for a 10-minute sample at 0.4 liters/min.

Reference: Saltzman, B. E. Colorimetric microdetermination of nitrogen dioxide in the atmosphere. Anal. Chem., 26, 1949-1955 (1954)

H. Hydrochloric Acid

The dissolved hydrochloric acid may be titrated either amperometrically (17,18) or turbidimetrically (19).

No rapid method for the detection of chlorides is available.

STANFORD RESEARCH INSTITUTE
ANALYTICAL SECTION METHOD

PRINCIPLES OF AMPEROMETRIC TITRATIONS

Introduction

1. An amperometric titration depends on the measurement of the diffusion current at an indicator electrode, and a change in the current corresponding to the stoichiometric end point. The potential across the electrodes is chosen to be on the diffusion current region of the current-voltage curve of one or both of the reacting substances. In this region the current is produced by reduction or oxidation of the diffusing substance and is proportional to the rate at which the substance diffuses to the electrode and hence to the concentration of the substance in the body of the solution.

Graphical Determination of End Points

2. A typical amperometric titration curve consists of two linear branches and an intermediate curving region. The first linear portion corresponds to the reaction of the substance being determined with the titrant; the second linear portion corresponds to an appreciable excess of titrant. The intermediate curved portion is due to solubility or massaction effects and is of no particular value for analytical purposes. The stoichiometric end point corresponds to the intersection of the extrapolated straightline portions of the curve.

Electrodes

3. Either a rotating platinum or a dropping mercury electrode may be used in amperometric titrations; the type used depends on the nature of the substance being titrated. The rotating platinum electrode is generally preferable for titrations made at applied potentials below the reduction potential or oxygen or for titrations employing an anodic reaction. For titrations where oxygen must be excluded, the conditions are reversed and the dropping mercury electrode is required.

Correction for Dilution

4. A correction for dilution is theoretically necessary to obtain a strictly linear relation between current and volume of reagent added. This correction is given by the equation:

$$i_c = i_o \frac{A + B}{A}$$

where

i_c = corrected current reading
i_o = observed current reading
A = original volume in titration cell, and
B = volume of titrant added to titration cell.

By titrating with a reagent at least ten times as concentrated as the solution being titrated, the correction becomes negligibly small. In practice, this is generally the case and the correction is omitted.

Depression of Solubility

5. When titrating with dilute solutions it is often necessary to add a nonaqueous diluent such as alcohol or acetone to lower the solubility of the precipitate and sharpen the end point. In general this is not necessary unless the normality of the titrating solution is 0.01 N or less.

ASM 31.01
APPARATUS
AMPEROMETRIC
March 10, 1950

STANFORD RESEARCH INSTITUTE
ANALYTICAL SECTION METHOD

APPARATUS FOR AMPEROMETRIC TITRATIONS

Introduction

1. The essential apparatus for amperometric titration consists of the following components:

(a) A source of DC potential having a range of 3 volts and means for reversing the polarity.

(b) A current indicating galvanometer having an adjustable shunt for controlling the sensitivity.

(c) A rotating platinum or dropping mercury electrode, with associated equipment.

(d) A reference electrode, having a sufficiently large area to be nonpolarizable. A saturated calomel electrode is commonly used.

(e) A titration cell.

The cell assembly employs a Fisher "Elecdropode" as the source of potential and as current indicator.

Source of DC Potential

2. Any convenient source of constant direct-current potential may be used in the amperometric apparatus. Means must be provided for adjusting the potential applied to the titration cell to any desired value between -3 and +3 volts. The Fisher "Elecdropode" (available from the Fisher Scientific Company, Pittsburgh, Pennsylvania), providing both a suitable DC source and a suitable current indicating meter, is recommended.

Current Indicating Meter

3. The current indicating galvanometer of the amperometric apparatus should be provided with shunt resistors to cover the sensitivity range 1/1 to 1/100. Suitable sensitivity ratios are 1/1, 1/5, 1/10, 1/20, 1/50, and 1/100. A meter with a minimum sensitivity of 0.01 microampere per millimeter scale deflection at the highest sensitivity setting is

desirable, but meters of lower sensitivity (e.g. microammeters) are suitable for many applications. The Fisher "Elecdropode" contains a satisfactory galvanometer and shunt.

Electrodes

4. (a) Stirring Motor. If a dropping mercury electrode is used, any small stirring motor is satisfactory. However, it is generally preferable to accomplish both deaeration and stirring by bubbling nitrogen gas through the solution. When a rotating platinum electrode is used the stirring motor should provide constant-speed stirring, since the current observed during titration depends to some extent on the speed of rotation of the electrode, and suitable means for connecting with the electrode and the external circuit by means of mercury contacts (metal brush contacts have variable resistance and give erratic operation). Either the Cenco cone-drive stirrer (Central Scientific Company, Chicago, Ill., Catalog No. 18805) or the Sargent cone-drive stirring motor (E. H. Sargent Co., Chicago, Catalog No. 76445) is satisfactory; these stirrers provide a range of constant speeds and have a small depression on top of the drive shaft which holds a drop of mercury, which provides a convenient contact to the metal housing of the stirrer.

(b) Rotating Platinum Electrode. A suitable electrode may be made as follows:

> Seal a short piece of 18-gage platinum wire into a piece of 6 mm soft glass tubing so that the wire extends about 2 to 5 mm on the outside wire at right angles to the tubing, and cut the tubing to the desired length (12 to 15 cm is generally satisfactory). Connect a copper wire firmly to the chuck or shaft of the stirring motor (in the Cenco or Sargent stirrers, this wire can conveniently be connected to a brass sleeve inside the chuck) and adjust the length of the wire so that it extends to the bottom of the glass tubing when the latter is placed in the stirrer chuck. Make contact between the copper and platinum wire by placing a drop or two of mercury in the tube.

(c) Dropping Mercury Electrode. The type of dropping mercury electrode used on polarographic apparatus may be used without modification on the amperometric apparatus. However, a means of stirring the solution must be provided either by a small stirring motor, or, preferably, by bubbling with nitrogen gas.

(d) Reference Electrode and Salt Bridge. A saturated calomel cell (of large area) of any conventional design may be used as the reference electrode in amperometric titrations. This electrode is connected to the titration cell by means of a special salt bridge, prepared as follows:

Obtain two glass tubes, each with one end closed by a sintered glass plug, the larger tube (sleeve tube) having an inside diameter of 8 to 9 mm and the smaller tube (plug tube) having an outside diameter such that when it is inserted in the sleeve tube, the annular space is 0.5 to 1.0 mm. These tubes can be of any convenient length, 10 to 15 cm being generally suitable. To the plug tube connect a two-foot length of 6 mm i.d. Tygon tubing. To the other (calomel cell) end of the Tygon tubing, connect a 10 to 15 cm piece of 5 mm i.d. glass tubing.

Prepare a solution of potassium nitrate by dissolving 20 g of KNO_3 in 100 ml of water and adding two g of agar-agar; warm until the agar-agar is dissolved. Clamp the two glass tubes connected to the Tygon tubing in a vertical position and fill the entire system with the warm solution, taking care that no bubbles remain in the column of solution. Close the open end of the glass tube with a small piece of very loosely rolled filter paper and allow to stand until the solution has jelled. Insert the filter paper-stoppered tube into the aqueous phase of the saturated calomel reference electrode.

For connection to the titration cell, fill the sleeve tube with a suitable electrolyte (usually saturated potassium nitrate or potassium chloride solution) and insert in the titration cell; the plug tube is then inserted into the sleeve tube.

Titration Cell

5. Temperature control is not critical in amperometric titrations as it is in polarographic work. Therefore ordinary beakers, 30 to 150 ml, are satisfactory for general work. For titrations at potentials more negative than 0.4 volt (the reduction potential of oxygen), a source of oxygen-free nitrogen is required for deaeration.

STANFORD RESEARCH INSTITUTE
ANALYTICAL SECTION METHOD

Determination of

CHLORIDE, BROMIDE, AND IODIDE ION
AMPEROMETRIC METHOD

Scope

1. This method is intended for the highly precise determination of low concentrations of chloride, bromide, and iodide ions in aqueous solutions. It is not directly applicable in the presence of sulfide, sulfite, permanganate, cyanide, thiocyanate, or phosphate ions, or in the presence of other substances which combine with silver or oxidize halide ion in dilute acid solution. The method has been designed for use as the final step in the determination of halogen in any type of organic or inorganic material after the halogen has been brought into solution as the halide ion. Since this method does not distinguish between the individual halides, total halide only is determined.

Outline of Method

2. The halide ion is titrated amperometrically in dilute nitric acid solution with silver nitrate solution, using a rotating platinum indicator electrode. The end point is determined graphically by plotting the volume of silver nitrate solution used against the observed current.

Reagents

3. (a) Gelatin Solution, 1%. To prepare, dissolve 1 g of c.p. gelatin in distilled water, add 1 ml of c.p. chloroform as a preservative, and dilute to 100 ml.

(b) Potassium Nitrate Solution, saturated.

(c) Silver Nitrate Solution, standard 0.1 N. For each liter of solution dissolve 17.0 g of c.p. silver nitrate in distilled water. Store in dark bottles. Standardize amperometrically, according to the procedure given in Section 6, against 0.1 to 0.15 g of reagent grade sodium chloride which has been previously dried to constant weight at 120°C.

(d) Silver Nitrate Solutions, standard 0.01, 0.001 N. Prepare by accurate dilution of the standard 0.1 N solution.

(e) Sodium Chloride Solution, standard 0.1 N. For each liter of solution dissolve 5.8 g of c.p. sodium chloride in distilled water. Standardize amperometrically, according to the procedure given in Section 6, against 0.1 N silver nitrate which has previously been standardized against a weighed amount of sodium chloride by the same procedure.

(f) Sodium Chloride Solutions, 0.01, 0.001 N. Prepare by accurate dilution of the standard 0.1 N solution.

(g) Acetone, c.p.

Apparatus

4. Amperometric Titration Apparatus. This method has been written for the Fisher "Elecdropode", equipped with a saturated calomel reference electrode and salt bridge, a constant speed stirring motor, a rotating platinum indicator electrode, and titration cells of various sizes.

Preparation of Apparatus

5. Fill the sleeve tube of the salt bridge about 1/4 full with saturated potassium nitrate solution, clamp the tube firmly and insert the plug tube. Connect the mercury electrode of the saturated calomel reference electrode to the "pool" terminal of the "Elecdropode"; connect the stirring motor case (which is connected by mercury contacts to the rotating platinum electrode) to the "drop" terminal. Set the voltage dial of the "Elecdropode" to zero.

Procedure

6. (a) By any suitable procedure obtain a neutral aqueous solution, free from interfering substances, in which all the halogen of the original sample is present as halide ion. Transfer the solution to a titration cell, adjust the volume, and add acetone, concentrated nitric acid and 1% gelatin solution according to Table I.

(b) Insert the rotating platinum electrode and the salt bridge assembly in the titration cell and adjust the sensitivity shunt of the galvanometer in accordance with the values given in Table I. Turn on the stirring motor and start adding silver nitrate solution, using a normality as shown in Table I. Add small increments of solution (e.g., 0.25 ml of 0.001 N, 0.10 ml of 0.01 N); after each addition of solution allow the galvanometer reading to become steady, and record that reading. Add silver nitrate solution and record the readings until the "bend" in titration curve is passed, and continue with a few more increments, recording the reading after each.

Table I

CONDITIONS OF HALIDE TITRATION

Condition		Expected Halogen Content, mg		
	Chlorine	0.0-0.5	0.5-5.0	5-50
	Bromine	0.0-0.8	0.8-8.0	8-80
	Iodine	0.0-1.2	1.2-12.0	12-120
Size of titration cell, ml		50	100	150
Volume before adding acetone, ml		10	25	100
Acetone, ml		20	25	0
Conc. nitric acid,ml		1	2	5
1% gelatin solution,ml		0.3	0.5	1.0
Galvanometer sensitivity		10X	20X	20-50X
Normality of titrant		0.001	0.01	0.1

(c) Plot the galvanometer readings against the corresponding volumes of silver nitrate solution added. Draw the best straight line through the points occurring well before the bend and through the points occurring well after the bend. Determine the volume of standard solution corresponding to the intersection of these lines.

> Note 1. To establish the two straight line branches of the titration curve accurately, it is necessary to obtain a sufficient number of points on each. With practice, two points are usually sufficient for the first branch; three or more points should be taken on the second branch after the end point (i.e. the curved portion) has been passed.

(d) If less than 0.002 milliequivalent of halide is found, repeat the determination, adding 5 ml of standard 0.001 N sodium chloride solution (standardized by titration under identical conditions) before adjusting the initial volume of the solution. From the total titration at the end point, subtract the titration corresponding to the added sodium chloride.

Calculation

7. (a) Calculate the total halide ion content of the aqueous solution analyzed by means of the following equation:

$$\text{Halide, meq.} = (V)(N)$$

where

V = volume of silver nitrate used, and
N = normality of silver nitrate used.

(b) Calculate the individual halogen content by means of the following equation:

$$\text{Halogen, \% W} = \frac{(H)(A)}{W}$$

where

H = milliequivalents of halide ion found
A = atomic weight of the halogen, and
W = weight of original sample milligrams represented by the aqueous solution analyzed.

Precision and Accuracy

8. Results should not differ from the mean by more than the following amounts:

Halide Content, meq.	Repeatability	Reproducibility
Less than 0.002	2% of mean	5% of mean
0.002 to 0.02	1%	2%
0.02 to 0.2	0.5%	1%
0.2 to 3	0.3%	0.5%

Determination of

HYDROGEN CHLORIDE
TURBIDIMETRIC METHOD

API Method 767-54

Scope

1. This method describes a procedure for the determination of hydrogen chloride (HCl) or other chlorides in waste gas.

Outline of Method

2. The chloride gas in the sample is absorbed in potassium hydroxide solution. The absorbed chloride is precipitated with silver nitrate, in the presence of alcohol, and the absorbance at 420 mμ is measured. The hydrogen chloride content in milligrams is obtained from a standard curve and calculated as volume percent.

Apparatus

3. (a) Sampling Train. Sampling train is shown in API Method 751, Fig. 751.5. The absorber should be constructed according to the specifications given in API Method 751, par.5e. For the gas meter, use a laboratory wet- or dry-gas type calibrated in cubic feet. A driven vacuum pump or an air, steam, or water ejector may be used for the aspirator.

(b) Photometer. A sensitive spectrophotometer or photoelectric colorimeter provided with a selective color filter which has a maximum transmittance at 420 mμ or less (Klett Filter No. 42, available from Klett Mfg. Co., 177 E. 87th St., New York, meets these requirements). The photometer must be equipped with absorption cells which allow light to pass through a layer of solution 40 mm to 50 mm thick.

Reagents

4. Unless otherwise indicated, it is intended that all reagents conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society where such specifications are available; otherwise, use best available grade:

(a) Methyl Alcohol. Methyl alcohol, 99.5 percent.

(b) Methyl orange Indicator Solution. Methyl orange indicator solution, 0.1 percent aqueous.

(c) Nitric Acid Solution. Nitric acid solution, 30 percent. To prepare 1 liter of solution, mix 345 ml of concentrated nitric acid (specific gravity 1.42) with 690 ml of distilled water.

(d) Potassium Hydroxide Solution. Potassium hydroxide solution, 5 percent.

(e) Silver Nitrate Solution. Silver nitrate solution, 0.1 N. To prepare 1 liter of solution, dissolve 17.0 g of silver nitrate ($AgNO_3$) in distilled water and dilute to 1 liter. Store in a dark bottle.

(f) Sodium Chloride. Sodium chloride, crystals, anhydrous. Dry at 900°F.

Sampling

5. Pass 1 to 2 cu ft of gas through the absorber containing 50 ml of 5% potassium hydroxide solution. Connect it, with rubber tubing, in a manner in which the gas will be pulled through from the sampling device at the stack, through absorbers, then through the meter, by means of a water aspirator or vacuum pump (see API Method 751). More samples may be required if experience shows the concentration of hydrogen chloride to be very low.

Procedure

6. (a) Quantitatively transfer the solution from the absorber to a 100-ml volumetric flask and make up to volume with the absorber washings. Pipette a 10-ml aliquot into a small beaker. Add 1 drop of methyl orange indicator solution. Make just acid with 30% nitric acid solution and add 3 additional drops. (Note 1). Boil for 2 min. Cool and transfer quantitatively to a 25-ml volumetric flask. Add 10 ml of methyl alcohol and make up to volume with 0.1 N silver nitrate solution. Mix thoroughly and let stand for 1 hour.

> Note 1. Excess of nitric acid is necessary to eliminate any interfering color from the indicator.

(b) Prepare a set of standards, using 5 ml of the original 5% potassium hydroxide reagent plus amounts of sodium chloride, equivalent to 0.00, 0.02, 0.04 mg of hydrogen chloride. Run these standards at the same time as the sample, following the procedure in Par. 6a (Note 2).

> Note 2. It is not possible to calibrate the instrument for this analysis; hence the necessity for running the sample and standard at the same time.

(c) Place the standard containing 0.00 mg of hydrogen chloride in the cell of the photometer and balance the instrument at zero absorbance. Determine the absorbance on the sample and on the remaining standards.

(d) On arithmetic graph paper plot the absorbance against the concentration of hydrogen chloride in the standards. From the absorbance determined on the sample and the graph, read and record the concentration of hydrogen chloride in the sample.

Calculation

7. Calculate the chloride content of the sample as hydrogen chloride by the following equation:

$$\text{Hydrogen chloride percent by volume} = \frac{0.0228\ E}{V}$$

where

E = hydrogen chloride, milligrams, read from reference chart
V = volume of gas sample, cubic feet, at 60°F and 1 atm.

$$0.0228 = \left[\frac{100\ (\%)}{1000\ (mg/g)}\right] \left[\frac{23.5\ (liters/mol)}{36.5\ (mol\ wt\ HCl)}\right] \left[\frac{100(flask, ml)}{10(aliquot, ml)}\right] \left[\frac{1}{28.32(liters/cu\ ft)}\right]$$

Precision

8. Duplicate results by the same operator should not differ by more than the following amounts:

Chloride, ppm	Repeatability, ppm
5.0	0.22
4.0	0.20
3.0	0.16
2.0	0.12
1.0	0.08
0.5	0.02
0.25	0.02

Reference: Luce, Denice, and Akerlund. Ind. Eng. Chem., Anal. Ed. 15, 365 (1943)

I. Hydrogen Cyanide

The titration of the absorbed hydrogen cyanide may be completed with amperometric methods (20) or by direct titration with silver nitrate.

A rapid method for the detection of hydrogen cyanide is the MSA detector. White (21) has described such an apparatus.

ASM 37.01
CYANIDE ION
AMPEROMETRIC
May 1, 1950

STANFORD RESEARCH INSTITUTE
ANALYTICAL SECTION METHOD

Determination of

CYANIDE ION
AMPEROMETRIC METHOD

Scope

1. This method is intended for the determination of low concentrations of cyanide ion in aqueous alkaline solutions. It is not directly applicable in the presence of large amounts of sulfide ion, iodide ion, or other ions which will precipitate with silver ion in dilute ammoniacal solutions.

Outline of Method

2. The cyanide ion is titrated amperometrically in dilute sodium hydroxide solution with silver nitrate using a rotating platinum indicator electrode. The end point is determined rapidly by plotting the volume of silver nitrate solution used against the observed current.

Reagents

3. (a) Potassium Nitrate Solution, saturated.

(b) Silver Nitrate Solution, standard 0.1 N. For each liter of solution dissolve 17.0 g of c.p. silver nitrate in distilled water. Store in dark bottles. Standardize amperometrically, against 0.1000 to 0.1500 g of reagent grade sodium chloride which has been previously dried to constant weight at 120°C.

(c) Silver Nitrate Solutions, standard 0.01, 0.001 N. Prepare by accurate dilution of the standard 0.1 N solution.

(d) Potassium Cyanide Solution, standard 0.1 N. For each liter of solution dissolve 6.5 g of c.p. potassium cyanide in 1 N. ammonium hydroxide. Standardize amperometrically according to the procedure given in section 6 against 0.01 N silver nitrate which has previously been standardized against a weighed amount of reagent grade sodium chloride by amperometric titration.

(e) Potassium Cyanide Solutions, 0.01, 0.001 N. Prepare by accurate dilution of the 0.1 N solution.

Apparatus

4. Amperometric Titration Apparatus. This method has been written for the Fisher "Elecdropode", equipped with a saturated calomel reference electrode and salt bridge, a constant-speed stirring motor, a rotating platinum indicator electrode, and titration cells of various sizes.

Preparation of Apparatus

5. Fill the sleeve tube of the salt bridge about 1/4 full with saturated potassium nitrate solution, clamp the tube firmly and insert the plug tube. Connect the mercury electrode of the saturated calomel reference electrode to the "pool" terminal of the "Elecdropode"; connect the stirring motor case (which is connected by mercury contacts to the rotating platinum electrode) to the "drop" terminal. Set the voltage dial of the "Elecdropode" to -0.23 volts.

Procedure

6. (a) By any suitable procedure obtain a 0.1 N sodium hydroxide aqueous solution free from interfering substances which contains all of the cyanide ion of the original sample. Transfer the solution to a titration cell and adjust the volume according to Table I.

(b) Insert the rotating platinum electrode and the salt bridge assembly in the titration cell and adjust the sensitivity shunt of the galvanometer in accordance with the values given in Table I. Turn on the stirring motor and start adding silver nitrate solution, using a normality as shown in Table I. Add small increments of solution (e.g. 0.25 ml of 0.001 N, 0.10 ml of 0.01 N); after each addition of solution allow the galvanometer reading to become steady, and record that reading. Add silver nitrate solution and record the readings until the "bend" in the titration curve is passed, and continue with a few more increments, recording the reading after each. (Note 1.)

Note 1. Amounts of cyanide ion which require the use of 0.1 N silver nitrate for titration can be determined in the presence of considerable ammonium ion. However, for lower concentrations of cyanide ion the presence of an excess of ammonium ion will cause high results. Accurate results are obtained if the solution is made alkaline with sodium hydroxide to a concentration of between 0.1 and 1 N.

Table I

CONDITIONS OF CYANIDE TITRATION

Condition	Expected Cyanide Ion Content, mg 0.0-0.8	0.8-8	8-80
Size of titration cell	50	100	150
Volume of solution to the titration	20	50	75-100
Galvanometer sensitivity	5X	10-20X	20-50X
Normality of titrant	0.001	0.01	0.1

(c) Plot the galvanometer readings against the corresponding volumes of silver nitrate solution added. Draw the best straight line through the points occurring well before the bend and through the points occurring well after the bend. Determine the volume of a standard solution corresponding to the intersection of these lines. (Note 2.)

> Note 2. To establish the two straight line branches of the titration curve accurately, it is necessary to obtain a sufficient number of points on each. With practice, two points are usually sufficient for the first branch; three or more points should be taken on the second branch after the end point (i.e. the curved portion) has been passed.

(d) If less than 0.002 milliequivalents of cyanide is found, repeat the determination, adding 5 ml of standard 0.001 N potassium cyanide solution (standardized by titration under identical conditions) before adjusting the initial volume of the solution. From the total titration at the end point, subtract the titration corresponding to the added cyanide.

Calculation

7. (a) Calculate the total cyanide ion content of the aqueous solution analyzed by means of the following equation:

$$\text{Cyanide, meq.} = (V)(N)\ 2$$

where

V = volume of silver nitrate used, and
N = normality of silver nitrate used.

HYDROGEN CYANIDE

Principle

Hydrogen cyanide is absorbed in sodium hydroxide solution, and sodium cyanide formed titrated against silver nitrate.

Apparatus

Bead bubbler, pump and flowmeter.

Reagents

Silver nitrate, 0.02 N. Dissolve 3.398 g A.R. silver nitrate in 1 liter water, either accurately prepared or standardized against sodium chloride.

Absorbing solution. Dissolve 5 g. A.R. sodium hydroxide in 100 ml water.

Potassium iodide solution. Dissolve 2 g A.R. potassium iodide in 100 ml water.

Method

Charge the bubbler with 15 ml absorbing solution and sample at 10 liters/min for 10 minutes.

Wash the contents of the bubbler into a titrating flask with water. Add 5 ml of potassium iodide solution and titrate the solution against 0.02 N silver nitrate until a permanent precipitate is produced. A black background assists in the titration. (Note 1).

> Note 1. The end point may be obtained with greater accuracy by performing the titration in semi-darkness with a condensed beam of light (such as from a microscope illuminator) passing through the solution.

Use a micro-burette and make "blank" determinations.

Calculation

1 ml 0.02 N silver nitrate solution is equivalent to 1.08 mg hydrogen cyanide.

Absorption Efficiency

One bubbler will absorb approximately 90 percent and two bubblers 99 percent of the hydrogen cyanide when sampling at 10 liters/min.

Sensitivity and Specificity

Using the procedure recommended 0.2 ml of 0.02 N silver nitrate solution is equivalent to approximately 2 ppm.

The method is specific for hydrogen cyanide.

Reference: The procedure is adapted from Cupples, H. L. Determination of hydrocyanic acid in air and in air-carbon dioxide mixtures. Ind. Eng. Chem., Anal. Ed. 65, 370 (1946)

J. Sulfur Trioxide

Sulfur trioxide or sulfuric acid mist is determined on the millipore filter by leaching the sulfuric acid with water. The subsequent analysis may be completed gravimetrically if the filters from three scrubber solutions are added to the same leach water. Otherwise the sulfuric acid may be determined turbidimetrically.

Snell and Snell (22) describe a titration method using diphenylcarbazide. The LACAPCD (23) describes a direct titration method using 0.0002 N sodium hydroxide. First and Silverman (24) also describe a direct titration method using the millipore filter.

ASM 9.01
SULFUR TRIOXIDE
GRAVIMETRIC
May 1, 1950

STANFORD RESEARCH INSTITUTE
ANALYTICAL SECTION METHOD

Determination of

SULFUR TRIOXIDE IN ABSORPTION TRAINS
GRAVIMETRIC PRECIPITATION METHOD

Scope

1. This method is intended for the determination of sulfur trioxide from gases which have been passed through a train of asbestos-packed Gooch crucibles and a caustic solution.

Outline of Method

2. Sulfur trioxide is determined by precipitation as barium sulfate after removal from the asbestos-packed Gooch crucibles by digestion with water and filtration. The sulfur trioxide passing the crucibles to the caustic scrubber is determined in the same way after boiling with acid to remove sulfur dioxide.

Reagents

3. (a) Barium Chloride Solution. Prepare by dissolving 100 g of c.p. barium chloride dehydrate in 1 liter of distilled water.

(b) Wash Solution. Saturate 1:300 hydrochloric acid with barium sulfate.

(c) Hydrochloric Acid, 6 N.

Procedure

4. (a) Place the Gooch crucibles from the absorption train in a 500-ml beaker and add sufficient water to permit thorough separation of the asbestos from the crucibles and dispersion of the mats to obtain the sulfur trioxide in the water. Digest the mixture at near boiling for 15 minutes and filter through a paper of medium porosity (Whatman No. 42). Adjust the volume to 175-200 ml by evaporation or dilution.

(b) Add 2 ml of concentrated hydrochloric acid, heat to boiling, and add from a pipet 10 ml of barium chloride solution dropwise or in a fine stream. Stir constantly during the addition and for 2 minutes afterwards. Allow the mixture to settle by digesting at 75 ±15°C for 1 hour on a hot plate and allowing it to stand an additional hour while cooling. Filter the supernatant liquid through a close-texture filter paper (Whatman No. 44). Wash the precipitate with water, first by decantation and then on the filter paper, until free from chloride ion.

(c) Transfer the paper and precipitate to a previously ignited and weighed porcelain or platinum crucible and dry in an oven at 110°C. Char the paper completely over a burner without igniting it, ignite at 500 to 550°C in a muffle furnace until all the paper is burned off, and finally heat at 750 to 800°C for 30 minutes. Cool the crucible to room temperature in a desiccator jar without drying agent and weigh.

(d) Determine the sulfur trioxide on the caustic scrubber solution after acidifying and boiling to remove sulfur dioxide, as described in a separate method for the determination of sulfur dioxide. (ASM 8.01.)

Calculations

5. Calculate the sulfur trioxide content of the sample by means of the following equation:

$$\text{Sulfur trioxide, ppm} = \frac{(A+B)(0.3429)(1000)}{(W)}$$

where

A = weight of barium sulfate in mg found in solution from Gooch crucibles
B = total weight of barium sulfate in mg found in caustic absorber after expelling sulfur dioxide, and
W = weight of original sample in grams represented by the aliquot taken.

K. Hydrogen Sulfide

Ammoniacal cadmium chloride is used to absorb hydrogen sulfide from the test atmosphere.

Various companies (14,25,26) provide rapid instruments for the detection of hydrogen sulfide. The Research Appliance Company's recorder continuously samples and analyzes the atmosphere. LACAPCD (23) and the Air Pollution Handbook (2) describe the methylene blue method for the determination of hydrogen sulfide.

ASM 5.01
HYDROGEN SULFIDE
IODATE
May 1, 1950

STANFORD RESEARCH INSTITUTE
ANALYTICAL SECTION METHOD

Determination of

HYDROGEN SULFIDE IN ABSORBER SOLUTIONS
IODATE TITRATION METHOD

Scope

1. This method is intended for the determination of low concentrations of sulfide ion in ammoniacal cadmium chloride absorber solutions. The cadmium sulfide precipitate is separated by filtration to prevent interference by sulfur oxides.

Outline of Method

2. The cadmium sulfide precipitated from the absorber solution is separated by filtration and washed with distilled water. The sulfide is oxidized with an excess of standard iodate solution in acid solution and the net volume determined by back titration with standard thiosulfate.

Reagents

3. (a) Potassium Iodate Solution, standard 0.01 N. Dissolve 0.7134 g of pure potassium iodate in distilled water and add 2 g of sodium hydroxide pellets. Then add 10 g of potassium iodide (free from potassium iodate). After complete solution of all salts, adjust to room temperature and dilute to 2 liters in a volumetric flask.

(b) Potassium Iodate, standard 0.005 N. Prepare by accurate dilution of the 0.01 N solution.

(c) Sodium Thiosulfate, 0.01 N. Dissolve about 5 g of sodium thiosulfate pentahydrate in 2 liters of freshly boiled and cooled distilled water. Store in a clean Pyrex bottle. To standardize this solution pipette 25 ml of the 0.01 N standard iodate solution into a 300-ml Erlenmeyer flask. Add 200 ml of water and 20 ml of hydrochloric acid. Allow to stand 1 minute and then titrate with the thiosulfate solution. As the end point is approached, add 10 ml of 0.2% starch solution and titrate carefully until the solution is colorless (the thiosulfate solution should be restandardized every 15 days).

(d) Sodium Thiosulfate, 0.005 N. Prepare before use by accurate dilution of 0.01 N standard thiosulfate.

(e) Starch Solution. Add a cold aqueous suspension of 2 g of soluble starch to 1 liter of boiling water. Cool to room temperature and store in a clean bottle.

Procedure

4. (a) Filter the absorber solution through a Whatman filter paper (No. 40). Wash twice with distilled water and transfer the paper to a glass-stoppered 125-ml Erlenmeyer flask. Add 50 ml of 1:10 hydrochloric acid and swirl once to mix thoroughly. Titrate immediately and rapidly with 0.005 N potassium iodate solution using a rapidly flowing buret until an excess of 1 or 2 ml has been added as indicated by the yellow color. (Note 1).

> Note 1. A rapidly flowing buret is considered as one which will empty by gravity in 60-70 seconds.

Cap immediately with a ground-glass stopper and shake vigorously to entrap any hydrogen sulfide in the atmosphere of the flask. Allow the potassium iodate buret to stand 1 minute after the titration before reading it. Add 10 ml of starch solution and titrate with freshly standardized 0.005 N sodium thiosulfate solution. Carry a blank through the whole procedure.

Calculation

5. Calculate the hydrogen sulfide in the sample by means of the following equation:

$$\text{Hydrogen sulfide, ppm} = \frac{(A-B)(17.04)(1000)}{(W)}$$

where

A = meq. of iodate used for the sample
B = meq. of thiosulfate used to back titrate, and
W = weight of original sample in grams.

L. Ozone

The Crabtree and Kemp method for ozone has been adopted by most investigators as a simple method. Phenophthalein and sodium indigo sulfate have also been used to determine atmospheric ozone.

Stressed rubber strips (28,29,30) and test papers (31) have been used as rapid and simple tests for the determination of ozone.

OZONE

Principle

Ozone is absorbed in acidified potassium iodide and the liberated iodine titrated with standard sodium thiosulfate.

Apparatus

Bead bubbler, pump, and flowmeter.

Reagents

Absorbing Solution. Dissolve 10 g A.R. potassium iodide in 100 ml water, and acidify with 5 ml glacial acetic acid. (The acidified absorbing solution is not stable and the acid should be added only when required for use).

Sodium Thiosulfate, 0.01 N. Dissolve 1.25 g A.R. sodium thiosulfate and 0.1 g sodium carbonate in 500 ml water and standardize against 0.01 N iodine.

Starch Solution. Mix 1 g soluble starch to a paste with water and pour with stirring into 200 ml boiling water. (Prepare a fresh solution each day.)

Method

Charge the bubbler with 15 ml absorbing solution and sample at 10 liters/min for 30 min. (Note 1).

> Note 1. Rubber connections should be reduced to a minimum, and where the use is unavoidable, they should be coated with shellac. It is advantageous to carry out the absorption away from light.

Immediately wash the contents of the bubbler into a titrating flask with water and titrate with 0.01 N sodium thiosulfate, using starch solution as indicator. Carry out "blank" determinations.

Calculation

1 ml 0.01 N sodium thiosulfate is equivalent to 0.24 mg ozone.

Absorption Efficiency

One bubbler will absorb more than 95 percent of the ozone when sampling at 10 liters/min.

Sensitivity and Specificity

Using the procedure recommended 0.1 ml 0.01 N sodium thiosulfate is equivalent to 0.04 ppm.

Any gas which will liberate iodine from potassium iodide will interfere, those most likely to be encountered being the oxides of nitrogen or hydrogen peroxide.

Reference: The procedure is a modification of "American Society for Testing Materials, Standards on Rubber Products," D470-41.

DETERMINATION OF OZONE CONCENTRATION IN AIR

The procedure described below can be used for determining the net oxidizing capacity of an atmosphere. The procedure is substantially that used by Crabtree and Kemp, Ind. Eng. Chem., Anal, Ed., 18, 769 (1946), for the determination of ozone. As of writing this procedure, it remains to be demonstrated whether any atmospheric contaminants interfere in the specific determination of the ozone concentration.

The determination is based on oxidation of iodide ion to free iodine in a neutral solution and subsequent titration of the iodine with thiosulfate. For convenience an electrometric end point is used. The principal reactions involved are:

$$O_3 + 2I^- + H_2O \longrightarrow I_2 + O_2 + 2OH^-$$

and

$$I_2 + 2S_2O_3^= \longrightarrow 2I + S_4O_6^=$$

The principal pieces of equipment are (1) a spray generating device for inducing intimate contact between the iodide solution and the atmosphere, (2) a pump for drawing the air stream through the spray device, (3) a meter for measuring the air rate, (4) a burette attached to the spray device to permit titrating the liberated iodine without the necessity of removing the solution to a separate container, (5) electrodes and an electrometric circuit for detecting the end point of the titration, (6) a trap to protect the pump from entrained liquid and to serve as a surge capacity in the line, and (7) a sponge rubber adsorber for removing ozone from an air stream for blank determinations and also for use during the actual time in which the titrating is carried out.

The spray generating device must be painted black or operated in a light proof cabinet to avoid photochemical release of iodine in the iodide solution by oxygen. If painted black, it is desirable to provide small clear spots on the front and back of the flask in which the spray is generated so that inspection of the jet and spray can be made. Also it is desirable to provide a clear vertical strip on the front of the upper liquid retaining chamber so that the liquid level in that chamber can be determined from time to time. The clear spots can be covered with black masking tape when not being used.

Titration using an appropriate electrometric circuit is possible because at an externally imposed voltage below the hydrogen overvoltage of the platinum electrode, at which polarization of the electrode occurs and no current flows, the presence of free iodine in the solution induces a current to flow. At low concentrations the current that flows is approximately proportional to the iodine concentration. Because there is a deviation from this proportionality at extremely low concentrations, it is preferable as will be indicated in the detailed procedure that follows, to titrate to a very small but measurable current rather than to no current flow.

The procedure for making an ozone concentration determination is described in the following steps:

1. For convenience first fill the reservoir of the 10 ml Koch-type burette with standard approximately 0.001 N sodium thiosulfate solution. Allow a small volume of the thiosulfate to flow into the spray flask to flush out any air bubbles in the burette tip. Drain the thiosulfate out of the flask.

2. With the apparatus arranged so that air will be drawn through the sponge rubber adsorber, start the air pump. A Welch rotary vane blower is a suitable pump. A pump with a pulsating suction is preferably not used with the apparatus. The rate of air flow through the device should be about 6000 cc/min (0.2 cfm). This is a scale reading of about 9 or 16 with a metal or glass ball respectively in a size 01-N-15 Flowrater.

3. By holding a small beaker up to the tube at the bottom of the spray flask and slowly opening the stopcock in the tube, about 75 ml of a neutral buffered potassium iodide solution can be drawn into the spray contacting device. Most of this liquid will be drawn up into the upper chamber. The volume should be sufficient to cover the platinum electrodes and the end of the vapor-liquid lift line.

   The composition of the neutral (pH 7) buffered potassium iodide solution is as follows. The solution should be kept in a light proof bottle to avoid iodine liberation.

KI	200 g	
$Na_2HPO_4 \cdot 12H_2O$	3.6 g	0.01 M
KH_2PO_4	1.4 g	0.01 M

   Dilute to approximately 1 liter

   A single charge of potassium iodide solution can be used for a good many ozone concentration determinations but from time to time during continued use, it is usually necessary to add small volumes of distilled water to the apparatus to make up for water evaporation losses and keep the electordes and vapor-liquid lift line covered. This distilled water can be added through the tube at the bottom of the flask in the same manner as the potassium iodide solution originally charged.

4. Check the adjustment of the electrometric circuit by throwing the toggle switch to "on" position and shorting across the binding posts. Adjust the 10,000 ohm potentiometer until the ammeter reading is exactly 50 microamps with the binding posts shorted. Subsequent readjustment of the potentiometer should not be necessary at least for several days of use, but the adjustment should be checked from time to time. If frequent readjustment is found to be required, the 4.5 volt battery may be run down and it may have to be replaced.

5. After adjusting the electrometric circuit, connect the leads from the platinum electrodes in the upper liquid retaining chamber to the binding posts. Be sure the toggle switch is in the "on" position. Note the ammeter reading which will probably be above two microamps. Slowly add 0.001 N thiosulfate solution from the burette until the ammeter reading decreases to two microamps. Brief experience with the apparatus will indicate the rate at which thiosulfate can be added without overshooting the desired reading.

6. A blank run can be made by allowing the air stream to continue to be drawn through the sponge rubber adsorber for a period of time, desirably at least half an hour. If ozone is being removed effectively by the sponge rubber, there should be no increase in the ammeter reading.

   To be a sound blank, the air stream being drawn into the sponge rubber should be from the same location as will be the stream in which it is desired to determine the ozone concentration. If this is done it may be possible to observe the effects of atmospheric contaminants on the analysis.

7. To make a determination of ozone concentration, be sure that the current reading is two microamps and then switch the air flow stream so that the sponge rubber adsorber is by-passed and the air to be analyzed passes directly into the spray contacting device for the period of sampling.

   At the normal air rate a concentration of ozone of 10 ppm by volume will result in a titration of about 1.5 ml of 0.001 N sodium thiosulfate for a thirty-minute run.

   It is convenient to note the ammeter reading as it increases during the sampling period inasmuch as this can be related quantitatively to the volume of titrating solution that will be required (and the ozone concentration).

   The electrometric circuit can be left on during a run. The flow of current does not cause any change in the iodine content of the solution. (Possibly iodine reacts with hydrogen at one electrode to form iodide as an equivalent amount of iodide is released at the other electrode to form iodine.) Also the flow of current is so small that the drain on the battery in the circuit does not cause rapid depreciation.

8. At the end of the period of sampling, the air flow should be switched to go through the sponge rubber adsorber and allow the air to continue to flow through the spray device.

9. Titrate the liberated iodine with the 0.001 N thiosulfate to an electrometric end point of a current of two microamps. As mentioned previously, experience will indicate the rate at which thiosulfate can be added without overshooting the desired end point.

   (For convenience in the event an end point is overtitrated or for other experimentation, wiring should be provided with the electrometric circuit so that iodine can be evolved from the solution by impressing a higher voltage across the electrodes than that used in the electrometric titration.)

   Depression of the push button will impose the higher voltage across the electrodes and liberate iodine regardless of the position of the toggle switch. With the 150 ohm fixed resistance connected in the circuit depression of the push button for one second will result in liberation of sufficient iodine to cause an increase in current flow as measured with the electrometric circuit of about three microamps (except that when there is an excess of thiosulfate in the solution an equivalent amount of thiosulfate is oxidized.)

10. The ozone concentration can be calculated according to the following formula which expresses the concentration in terms of parts per 100 million of ozone by volume.

$$\text{Ozone conc. pphm by vol} = \frac{\dfrac{(\text{Vol. thio.})(\text{N thio})(\text{Vol } O_3)}{(2 \text{ equiv. thio/mol } O_3)(\text{mol} O_3)} \text{ k evap.}}{(\text{Air rate})(\text{Time}) \times 10^{-8}/\text{pphm}}$$

$$\text{Ozone conc. pphm by vol} = 12 \times 10^{8} \frac{(\text{ml thio})(\text{N thio}) \text{ k evap.}}{(\text{cc/min air})(\text{Min. of test})}$$

   It is desirable to include a factor "k" in the calculating to correct for evaporation of iodine from the solution during the run time. Crabtree and Kemp have found the evaporation loss to be about 1% for every five minutes of run length. Therefore, the factor k is 0.01 for every 5 minutes of run time.

M. Carbon Monoxide

It is suggested that the carbon monoxide be determined using gel indicators (32,33,34) supplied by the Mine Safety Appliance Company.

CARBON MONOXIDE

Principle

The air sample is collected in suitable vessels and then passed over heated iodine pentoxide, when the carbon monoxide is oxidized to the dioxide and iodine liberated. The iodine is absorbed in potassium iodide solution and determined volumetrically.

Appratus

Iodine Pentoxide Tube. A Pyrex glass U-tube. Before the neck pieces are sealed on, charge the U-tube with alternate half-inch layers of glass wool and iodine pentoxide, (prepared as described in Note 1) so as to contain 30 to 40 g of the latter. If the pentoxide is insufficiently dried, iodine is produced whether carbon monoxide is present or not. The material in the tube should not be packed too tightly, and space should be left between the end of the filling and the open ends of the tube to avoid heating the pentoxide unduly when sealing on the neck pieces. The temperature of the pentoxide should not be raised above 250°C during this process. A freshly charged tube should be heated at 200°C for eight hours with carbon monoxide-free gas passing, and then at 150°C until the blank is sufficiently low. The efficiency of the filling should be checked every three months by the analysis of known concentrations of carbon monoxide (prepared as described in Note 2).

> Note 1. The Preparation of Iodine Pentoxide. Place 600 ml fuming nitric acid (S.G. 1.516-1.520) in a long-neck 1 liter flask in a water bath maintained at a temperature of 70 to 75°C. At higher temperatures, large amounts of iodine sublime on the neck of the flask. Allow the acid to reach the temperature of the bath. Add C.P. Iodine (finely ground) slowly, 1 g at a time until 120 g have been added. Allow the violent evolution of oxides of nitrogen to subside and the liquid to become clear enough to see through before the next addition of iodine. The process takes about six hours. Raise the bath temperature to 80-85°C and maintain at this temperature until the reaction ceases (about a further 2 hours).
>
> Pour off the acid and add 400 ml water. Boil to dissolve the solid matter. Transfer the liquor to a bolt-head flask and boil off the liquid until iodic acid starts to separate. The volume should be about 200 ml. Cool and allow to stand, preferably overnight, until the supernatant liquid is clear. Pour off the liquid and dissolve the solid in 80 ml hot water.
>
> Place the solution in an evaporating basin and heat slowly on a sand bath to a temperature of 175-200°C. Do not allow the temperature to rise above 200°C. Continue heating until the solid is dry, keeping it stirred continuously. The yield should be about 120 g iodine pentoxide.

Note 2. The Preparation of Carbon Monoxide. Heat 50 ml A.R. sulfuric acid in a 250 ml "Quick-fit" flask, fitted with a side-arm tube and dropping funnel, in an oil bath at 120-150°C for 1 hour. Attach the side arm to a gas reservoir.

Add 6 ml 90% formic acid drop by drop, allowing the reaction to subside before the addition of the next drop. Collect the gas in the reservoir after the air has been displaced.

Check the purity of the gas sample using a standard gas analysis apparatus.

Oven. An electrically heated oven which can be maintained at 150°C.

Absorption Vessel. An absorption vessel of the design described.

Purification Train. The purification train should consist of the following absorbents: (a) concentrated sulfuric acid and chromic acid; (b) soda lime; (c) magnesium perchlorate used as a desiccant; (d) activated charcoal.

Sampling Vessel. A liquid displacement gas collector is used, consisting of a Winchester fitted with a rubberbung, and inlet and outlet tubes each fitted with a pinch-cock.

Pump. A pump is required for drawing the air through the apparatus at about 1-5 liters/hour.

Care should be taken with the use of grease on the ground-glass connection between the iodine pentoxide tube and absorption vessel, as it is likely to absorb iodine. It is also desirable for the connections from the furnace to the absorption vessel to be as short as possible to avoid condensation of iodine. The upper portion of the iodine pentoxide tube should not project far from the furnace for the same reason.

Reagents

Nitrogen. Compressed nitrogen gas for purging the apparatus and for determining the "blank". Alternatively a second iodine pentoxide assembly may be set up and air which has passed through this be used in place of nitrogen.

Potassium Iodide, 10 percent. Dissolve 10 g A.R. potassium iodide in 100 ml water.

Sodium Thiosulfate, 0.1 N. Dissolve 25 g A.R. sodium thiosulfate and 0.1 g anhydrous sodium carbonate in water, make up to 1 liter and standardize against pure iodine.

Sodium Thiosulfate, 0.002 N. Dilute 10 ml 0.1 N sodium thiosulfate to 500 ml with water daily as required.

Starch Solution. Mix 1 g soluble starch to a paste with water and pour, with stirring, into 200 ml boiling water. (Prepare a fresh solution each day.)

Method

Heat the iodine pentoxide tube at a temperature of 150-160°C and pass air free from carbon monoxide, or nitrogen through the tube at a rate of between 1 and 5 liters/hr. Before using the apparatus for analysis of an air sample, obtain a satisfactory "blank" reading on drawing gas, free from carbon monoxide, through the apparatus for the same time and at the same rate as for the sample.

Take a 2-liter air sample by aspiration and connect the sample to the assembly. Pass the air sample through the assembly, and subsequently purge the apparatus for 60 min with carbon monoxide-free gas in order to sweep over all the liberated iodine. Titrate the iodine collected in the absorption vessel with 0.002 N sodium thiosulfate using starch solution as indicator.

Calculation

1 ml 0.002 N sodium thiosulfate is equivalent to 0.14 mg carbon monoxide.

Sensitivity and Specificity

Using the procedure recommended, 0.1 ml of 0.002 N sodium thiosulfate is equivalent to 6 ppm. For concentrations in excess of 1000 ppm, it is recommended that the sample be diluted with carbon monoxide-free air before estimation by this method.

The purification train removes the following substances which interfere: sulfur dioxide, hydrogen sulfide, unsaturated hydrocarbons, higher paraffins and organic vapors, petrol vapor, water vapor, and formaldehyde.

Methane, ethane and hydrogen have very little effect on the iodine pentoxide at 150°C.

References: The method for the estimation of carbon monoxide is adapted from Lunge, G. and Ambler, H. R. Technical Gas Analysis, Gurney and Jacksons, London (1934), and Jacobs, M. B. The Analytical Chemistry of Industrial Poisons, Hazards and Solvents, Interscience Publishers, Inc., New York (1944). The preparation of iodine pentoxide is taken from Archibald, E. H. The preparation of pure inorganic substances. John Wiley and Sons, New York (1932), and King, A. Inorganic preparations, Thomas Murby, London, (1936).

N. Organics

The organic component of the test atmosphere will be difficult to analyze directly without resorting to a freeze-out technique. It might be possible, however, to detect the benzene component of the test atmosphere; if benzene is in the correct concentration range it could be assumed that the total organics are in the correct range. In fact, it might be advisable to assume the correct concentration range for the total organics without analysis of the atmosphere.

The Mine Safety Appliance Company has equipment available for the detection of benzene. Maffett, et al (35) describe a method for the determination of microamounts of benzene and toluene in air. Other methods absorb organic material in solvents such as dodecane or isooctane (spectroscopic grade) and analyze the resultant solution with ultraviolet.

Recent research at Stanford Research Institute has indicated some success in the use of gel indicators for saturated hydrocarbons -- normal, cyclic, substituted, and branched-chain hydrocarbons. A sensitivity limit of 5 ppm for a 60-cc sample was obtained using a gel indicator of the following composition: 10.6 g silica dioxide (Davison No. 950), 0.25 g iodine pentoxide, and 2.5 ml fuming sulfuric acid (65% SO_3).

ASM 406.01
ORGANIC GROUP
ULTRAVIOLET
May 1, 1950

STANFORD RESEARCH INSTITUTE
ANALYTICAL SECTION METHOD

ORGANIC GROUP ANALYSIS
ULTRAVIOLET ABSORPTION METHOD

Scope

1. This method is intended for the characterization of those organic compounds which absorb in the ultraviolet region of the spectrum. The upper limit of concentration is obtained.

Outline of Method

2. Absorption spectra of dodecane samples are determined at a series of predetermined wave lengths. From the data furnished by the API Project No. 44 (National Bureau of Standards) limiting concentrations of certain compounds and groups of compounds are determined.

Apparatus

3. Ultraviolet Spectrophotometer. A Beckman Quartz Spectrophotometer, Model DU, equipped with an ultraviolet source and 1-cm fused quartz cells, is suitable.

Procedure

4. (a) Determine the volume of the dodecane scrubber solution and place a portion in the 1-cm quartz cell. Place some of the original dodecane used in sampling in the reference cell. Take transmission readings at each 5 mμ from as short a wave length as possible up to 300 mμ and then at each 10 mμ up to 400 mμ. If a transmission less than 10% is obtained on any portion of the spectrum, dilute the absorber solution with dodecane to obtain transmission measurements of at least 10%. (Note 1.)

Note 1. It is not necessary to repeat those measurements which gave an original transmission of over 10%.

Calculations

5. (a) Calculate the optical density of the solutions at each wave length, using the following equation. (Note 2.)

$$\text{Optical density} = \frac{\log 100}{T} \times \frac{1000}{V} \times F$$

where

T = transmission observed at given wave length
V = original volume of absorber solution, and
F = dilution factor where transmission below 10% was observed.

> Note 2. Optical density as used herein is arbitrarily taken as the density obtained from 1 liter of the absorbing solution in the cell path of 1 cm. It is calculated thus for convenience in using the table which follows.

(b) From the values obtained in 5(a) use Table I to find the upper limit of concentration of each compound or group of compounds in the scrubber solution. (Note 3.)

Table I

Type of Compounds	Wave Length, mμ	Optical Density for 0.01 g/liter
Alkyl benzenes	260	0.015
Biphenyls	260	0.8
Pyridine	260	0.2
Alkyl naphthalenes	285	0.3
Diolefins	235	3.0
Aniline	235	1.0
Thiophene	235	0.7
Nitrobenzene	235	0.7
Styrene	235	1.1
Anthrocene	350	0.2
Acrolein	350	0.0035

> Note 3. These data are taken from API Project No. 44 conducted by National Bureau of Standards.

(c) Calculate the upper limit of concentration of the substances listed in the table as ppm of the gas stream sample by means of the following equation:

$$\text{Organic substance in gas, ppm} = \frac{(A)(B)}{(W)1000}$$

where

A = upper limit of conc. of organic substance or group in mg/ml of absorber solution
B = volume of the absorber solution, and
W = weight of the gas sample taken for analysis.

ASM 406.02
ORGANIC GROUP
ULTRAVIOLET
June 15, 1950

STANFORD RESEARCH INSTITUTE
ANALYTICAL SECTION METHOD

ORGANIC GROUP ANALYSIS
ULTRAVIOLET ABSORPTION METHOD

Scope

1. This method is intended to set an upper limit of concentration for several possible types of organic compounds which absorb in the ultraviolet region of the spectrum. It is not intended to be used as an absolute measure of any particular compound unless it is known by other means that a definite compound is present.

Outline of Method

2. Absorption spectra of dodecane samples are determined at a series of predetermined wave lengths. From the data furnished by the API Project No. 44 (National Bureau of Standards) limited concentrations of certain possible compounds and groups of compounds are determined.

Apparatus

3. Ultraviolet Spectrophotometer. A Beckman Quartz Spectrophotometer Model DU, equipped with an ultraviolet source and 1-cm fused quarts cells, is suitable.

Reagents

4. Dodecane. The dodecane used to absorb organic compounds from gases should be free from impurities which absorb in the region of interest. If a satisfactory supply is not available, technical material can usually be used after passing through a column of silica gel. If another solvent is used, reserve a portion of unused solvent for a blank.

Procedure

5. Determine the volume of the dodecane sample and place a portion in the 1-cm quartz cell. Place some of the original dodecane used in sampling in the reference cell. Take optical density readings at each 10 mμ from 400 mμ down to 300 mμ and then at each 5 mμ down to as short a wave length as possible. When an optical density of more than 0.1 is obtained, dilute the absorber solution with dodecane to obtain optical densities below 1.0. Do not repeat those measurements which gave an original optical density of less than 1.0. (Note 1.)

Note 1. The readings were started at a long wave length because samples usually increase rapidly in absorption at shorter wave lengths and the point for dilution is more readily obtained.

Calculations

6. Calculate the upper limit of total moles for a selected group of compounds, using the molecular absorption coefficients given in Table I.

$$\text{Organic compound (upper limit in moles)} = \frac{(D)(V)(F)}{(E)\ 1000}$$

where

D = optical density observed at selected wave length for the particular group of compounds
V = original volume of absorber solution
F = dilution factor where optical density greater than 1.0 was observed, and
E = molecular absorption coefficient from Table I.

Table I

TABLE OF MOLECULAR ABSORPTION COEFFICIENTS FOR CALCULATION OF UPPER LIMITS FROM ULTRAVIOLET DATA

Group of Compounds and Number	Wavelength	Molecular Absorption Coefficient
A Diolefins (4)	230	14,500
	235	5,600
	240	660
B Thiophenes (3)	235	5,000
	240	4,200
C Phthalic acids (3)	235	6,600
	280	1,140
D Alkyl biphenyls (4)	240	8,400
E Styrenes (3)	250	13,000
	240	14,500
F Nitrobenzene (1)	250	8,800
G Pyridines (4)	250	1,600
H Anthracenes (3)	250	90,000
	360	3,400
I Benzene (1)	250	85
J Other alkyl benzenes (49)	260	150
K Chloro benzenes (4)	260	145
L Diphenyl alkanes (3)	260	460
M Alkyl tetrahydronaphthalenes	260	240
N Alkyl naphthalenes (14)	270	4,200
O Anilines (2)	290	1,600
	240	7,600

Molecular absorption coefficients calculated from the "Catalog of Ultraviolet Spectral Data" by the API Project 44, National Bureau of Standards, as of September 30, 1948. The values for molecular absorption are the minimum values for a particular group. The maximum value for a particular group at the selected wave length is no greater than twice this value and usually much closer to the minimum value. Where more than one wave length is given, the first is preferred but the one giving the smaller amount of organic material should be used.

O. Solids

The sampling and analysis of solids in the test chamber is also difficult because of the limited volume in the test chamber. If all the solids in the test chamber were sampled, the total collection would be slightly less than 15 milligrams. If a tenth of the volume were sampled, the weight of solids would amount to about 1.5 milligrams. An emission spectrograph could be taken on this sample by the copper spark method (36). The following metals could not be determined with any degree of precision: arsenic, barium, cadmium, cobalt, and mercury.

The Mine Safety Appliance Company describes a dust and fume sampler. Other investigators (37,38) describe other methods for the measurement of dusts in the atmosphere.

The procedures used by the Taft Sanitary Engineering Center for the Community Air Pollution Program are appended.

ROBERT A. TAFT SANITARY ENGINEERING CENTER

Community Air Pollution Program   Chemical Research & Development Section

AIR PARTICULATE MATTER SAMPLES COLLECTION AND PREPARATION FOR ANALYSIS

Twenty-four hour samples are collected on weighed 8 x 10 in. sheets of flash-fired glass-fiber filter web using a high volume sampler designed for this type of filter medium.

After collection of the sample the filter is again weighed to the nearest milligram. It may be necessary in some cases to dry the sample in a desiccating chamber prior to weighing to remove extra moisture.

The sample is divided as follows:

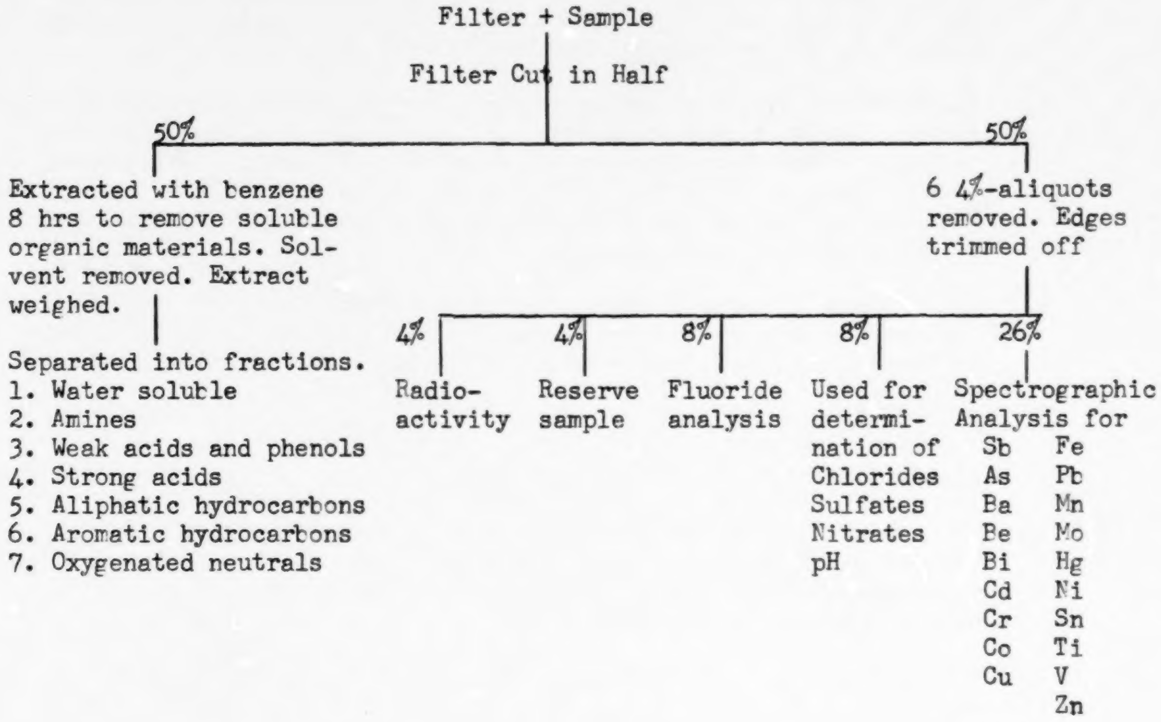
1. First cut sample into equal halves, one of which is set aside for removal of organic matter.

2. Trim the edges from the second half.

3. Using a die 1-3/4 in. in diameter, cut out six circles from the trimmed-half sample. The remainder which represents 26% of the original sample may be used for the spectrographic determination of metals.

4. The circles each of which represents 4% of the original sample are used as follows: two circles are extracted and used for the determination of chlorides, sulfates, nitrates and pH, two circles are used for the determination of fluorides, one circle is used for measurement of radioactivity,and the remaining circle is held in reserve. These aliquots may be used for other analyses if desired.

Flow Sheet Showing Analytical Procedures for Analysis of Air Particulate Matter Collected on Fiber Glass Filters


Filter + Sample
Filter Cut in Half
50%
50%
Extracted with benzene 8 hrs to remove soluble organic materials. Solvent removed. Extract weighed.
Separated into fractions.
1. Water soluble
2. Amines
3. Weak acids and phenols
4. Strong acids
5. Aliphatic hydrocarbons
6. Aromatic hydrocarbons
7. Oxygenated neutrals
6 4%-aliquots removed. Edges trimmed off
4%
4%
8%
8%
26%
Radioactivity
Reserve sample
Fluoride analysis
Used for determination of Chlorides Sulfates Nitrates pH
Spectrographic Analysis for
Sb
As
Ba
Be
Bi
Cd
Cr
Co
Cu
Fe
Pb
Mn
Mo
Hg
Ni
Sn
Ti
V
Zn

THE EXTRACTION OF ORGANIC MATERIALS FROM PARTICULATE MATTER COLLECTED ON GLASS FIBER FILTERS

1. Fold or roll the sample into a bundle to prevent loss of material during the extraction procedure and to allow it to be easily introduced into the extractor. Tie bundle with fine copper wire.

2. Place the sample in a Soxhlet extractor and extract with the desired solvent for a minimum of 8 hrs. If convenient, a 12-hr extraction period may be used. However, an 8-hr, rapidly cycling extraction removes approximately 95% of the amount removed by a 12-hr extraction. The National Air Sampling Network samples are extracted with benzene at the time this procedure was written.

3. The extract is concentrated to a small volume (5 ml) by evaporation. This can be done by means of a closed distillation system or simply by heating very cautiously on a hot plate in a well ventilated hood.

4. Filter the concentrated extract through a medium porosity Corning fritted-glass filter into a weighed test tube or flask, using a Fisher Filtrator or similar apparatus. Wash the original container and filter at least twice with small amounts of acetone. Small volumes of acetone efficiently remove the organic materials and prevent accumulation of organic matter in the filter which may clog the pores of the filter. This procedure enables one to filter several samples in sequence with no chance of contamination.

5. The remainder of the solvent is removed by heating in an oven maintained slightly below the boiling point of the solvent. All electrical controls of the oven must be outside the oven, otherwise an explosion is likely to result due to sparking of the controls. The solvent may also be removed "in vac" but boiling may occur resulting in loss of material.

6. Weigh the sample after the last of the solvent has been removed. If desired, the samples may be reheated until they reach a constant weight.

Selection of Solvent for Removing Organic Matter

Several solvents have been used for removing organic materials from air particulate samples. The choice of solvent must be based on the interest of the individual worker. Extraction with acetone will result in the removal of more organic matter from the sample than would the extraction with benzene, ethyl ether, chloroform, etc., but the extracted material will not completely redissolve in any solvent. Benzene and cyclohexane extracts redissolve readily and are well suited for infrared examination. Polycyclic compounds are effectively removed by benzene or cyclohexane extration. Chloroform is a very satisfactory solvent which removes only slightly less material than does acetone.

No single solvent will remove all of the organic material from the filter. There may be some advantage in extracting first with benzene, second with acetone and finally with ethanol. Such an extraction would remove a large amount of organic material giving fractions that could be used for different isolation procedures such as chromatography.

When using acetone or ethanol, considerable inorganic material will also be removed. This is a disadvantage and must be considered when choosing a solvent.

Use of ethyl ether, benzene, acetone, etc., has been reported in the literature. No standard technique has been adopted for removal of organic matter from air particulate matter as all work in this field has been independent in nature.

DETERMINATION OF WATER SOLUBLE SULFATES IN AIR PARTICULATE MATTER COLLECTED ON GLASS FIBER FILTER WEBS

Extraction of Water Soluble Sulfates from the Sample

1. Place an 8% aliquot of the sample into a 125-ml flask, add 50 ml distilled water.
2. Reflux 1-1/2 hrs. Cool.
3. Filter through Whatman No.1 paper.
4. Repeat the extraction using 10-15 ml water and heating only a few minutes without a condenser.
5. Filter the solution through the same filter, washing the flask and filter until the total volume of filtrate is 80 ml. Mix the filtrate thoroughly. Store in a clean rubber-stoppered bottle.
6. This solution may be used for the determination of chlorides, nitrates, sulfate, and pH. Each ml of the solution is equivalent to 1% of the sample. Note: A 4% aliquot of the sample may be extracted giving a volume of 40 ml.

Determination of Sulfates

1. Transfer a 10- or 20-ml aliquot of the solution into a graduated cylinder or a test tube graduated at 25 ml. The size of the aliquot to be used has to be established by preliminary tests on samples from different locations.
2. Add 1 ml 10 N hydrochloric acid, 4 ml of the glycerine-alcohol solution, and dilute to 25 ml if necessary. Mix thoroughly.
3. Add approximately 0.25 g barium chloride crystals and mix until the crystals are dissolved.
4. Allow to stand 40 min.
5. Read in a spectrophotometer at 500 mμ against a reagent blank. Any spectrophotometer accommodating cuvettes with a light path of 25 to 50 mm should be satisfactory.
6. Determine the sulfate content of the sample by referring to the calibration curve.
7. Matched, 25-mm, screw cap tubes may be used for this determination if they fit the spectrophotometer being used. A spectrophotometer adapted to the use of 20 mmx40 mm rectangular cuvettes is to be preferred on account of its greater flexibility.

Calibration of the Spectrophotometer

1. Prepare a stock sulfate solution using a dry sulfate of high quality.

2. From the stock solution prepare working standards equivalent to 100, 300, 500, 700, and 1000 μg sulfate per 10 ml of solution.

3. Pipette replicate 10 ml portions of each standard into graduates or test tubes graduated at 25 ml.

4. Follow the procedure outlined in Determination of Chlorides, starting at step 2. All readings should be made against a reagent blank. Repeat the calibration until a satisfactory calibration curve is obtained.

5. Plot percent transmittance against amount of sulfate on semi-log paper. A straight line should be obtained.

Reagents

1. 10 N hydrochloric acid. Dilute 80 ml of concentrated acid to 100 ml with distilled water.

2. Glycerine-alcohol solution. Mix 1 volume of glycerine with 2 volumes of 95% ethanol.

3. Barium chloride crystals. High quality 20-30 mesh crystals.

4. Standard sulfate. Any high grade soluble sulfate may be used.

DETERMINATION OF WATER SOLUBLE CHLORIDE IN AIR PARTICULATE MATTER COLLECTED ON GLASS FIBER FILTER WEB

Extraction of Water Soluble Chlorides from Sample

1. Place an 8% aliquot of the sample into a 125-ml flask, add 50 ml distilled water.
2. Reflux 1-1/2 hrs. Cool.
3. Filter through Whatman No. 1 paper.
4. Repeat the extraction using 10-15 ml water and heating only a few minutes without a condenser.
5. Filter the solution through the same filter, washing the flask and filter until the total volume of filtrate is 80 ml. Mix the filtrate thoroughly. Store in a clean rubber-stoppered bottle.
6. This solution may be used for the determination of chlorides, nitrates, sulfates, and pH. Each ml of the solution is equivalent to 0.1% of the sample. Note: A 4% aliquot of the sample may be extracted giving a volume of 40 ml.

Determination of Chlorides.

1. To 20 ml of the water extract add 1 drop of the p-nitrophenol solution.
2. Add N nitric acid drop by drop until the solution becomes colorless.
3. Over-lay with 2 ml silver nitrate reagent.
4. Dilute to 25 ml with distilled water.
5. Stopper and mix by inversion 6 times.
6. Allow to stand exactly 30 min, then read in a spectrophotometer at 500 mμ against a reagent blank. The solution should be stored in the dark for the 30 min period and the spectrophotometric measurement should be carried out in a dimly lighted room in order to avoid reduction of the silver chloride which takes place in bright light.
7. Determine the amount of chloride in the sample by referring to the standard curve.

Calibration of Spectrophotometer

1. Prepare a stock chloride solution using a dry sample of either pure sodium or potassium chloride. 0.210 g KCl/liter is equivalent to 100 µg chloride/ml.

2. Prepare a set of working standards containing 20, 50, 100, and 200 µg per 20 ml by properly diluting the stock solution.

3. Follow the procedure outlined above using replicate samples of each of the standards prepared above. Repeat if necessary to give adequate precision.

4. Plot the results obtained on semi-log paper, µg chloride against percent transmittance. The result should be a straight line. It is usually desirable to use the total micrograms in the sample which is 50 times the amount used in the calibration procedure as it facilitates interpretation of the spectrophotometer reading.

Reagents

1. 3% para-nitrophenol in 9% ethanol.

2. N nitric acid.

3. Sodium or potassium chloride for standards

4. Silver nitrate reagent - 1 g silver nitrate dissolved in 20 ml distilled water, add 1 ml nitric acid, then dilute to 100 ml. Store in a dark bottle.

This determination may be carried out on samples collected in an impinger using 0.1 N sodium hydroxide as a collecting medium.

1. Evaporate the solution to 5-10 ml, add 1 drop of p-nitrophenol solution, then proceed beginning at Determination of Sulfates, paragraph 2.

Note: It may be desirable to use redistilled water and nitric acid if the blank shows much turbidity.

Strong light must be avoided while carrying out this procedure.

All readings should be made against a reagent blank.

Bromide, iodide, thiocyanate, cyanide, ferrocyanide, ferricyanide, sulfide and thiosulfate ions will interfere in this determination by precipitating as silver salts.

DETERMINATION OF NITRATES IN AIR PARTICULATE MATTER COLLECTED ON GLASS FIBER FILTER WEB

(Modified method of H. Barnes, Analyst 75,388 (1950))

Extraction of Nitrates from Sample

1. Place an 8% aliquot of the sample into a 125-ml flask, add 50 ml distilled water.

2. Reflux 1-1/2 hrs. Cool.

3. Filter through Whatman No. 1 paper.

4. Repeat the extraction using 10-15 ml water and heating only a few minutes without a condenser.

5. Filter the solution through the same filter, washing the flask and filter until the total volume of filtrate is 80 ml. Mix the filtrate thoroughly. Store in a clean rubber-stoppered bottle.

6. This solution may be used for the determination of chlorides, nitrates, sulfates, and pH. Each ml of the solution is equivalent to 0.1% of the sample. Note: 4% aliquot of the sample may be extracted giving a volume of 40 ml.

Determination of Nitrates

1. To a 2-ml aliquot of the above solution in a 25-mm test tube, add 3 ml of water and 15 ml of 85% sulfuric acid. Mix and allow to cool.

2. Add 1 ml of the xylenol reagent. Mix.

3. Heat in a 60° water bath for 30 min. Cool.

4. Transfer the contents of the tube to a 250-ml separatory funnel rinsing the tube with distilled water. A total of 80 ml of water should be added to the separatory funnel.

5. Add 10 ml of toluene to the separatory funnel. Shake fairly vigorously for at least 2 min. A standard shaking procedure should be adopted to insure consistent results. Too vigorous shaking must be avoided to prevent emulsification.

6. Allow to stand for 15 min then run off and discard the lower layer.

7. Wash the toluene with 20-25 ml of water, shake gently and allow to settle for a few minutes.

8. Completely run off the lower layer and discard.

9. Add 10 ml of 0.4 N sodium hydroxide solution and shake gently for 5 min.

10. Allow to stand until the lower layer becomes clear then filter the lower layer through Whatman No. 1 paper into a clean and dry cuvette.

11. Read the transmittance of the solution at 435 mμ against a reagent blank prepared in the same manner.

12. Obtain the concentration of the nitrate in the sample by referring to the calibration curve.

Calibration of the Spectrophotometer

1. Prepare a stock nitrate solution containing 100 mg of nitrate per liter. 163 mg KNO_3 per liter.

2. Prepare working standards containing 10, 20, 40, 60, 80, and 100 μg per 5 ml by properly diluting the stock solution.

3. Pipette 5 ml portions of the working standards into test tubes and add 15 ml of 85% sulfuric acid solution. Mix and cool.

4. Proceed as outlined in Determination of Nitrates, starting at step 2.

5. Read the transmittance of the solution at 435 mμ against a reagent blank.

6. Plot transmittance vs microgram nitrate per 5 ml of solution on semi-log paper.

Reagents

1. Xylenol reagent. 1 Percent by volume of 2.4 xylenol in glacial acetic acid.

2. Sulfuric acid,85 percent. Add 480 ml of conc. sulfuric acid with care to 117 ml water.

3. Sodium hydroxide, 0.4 N solution.

Notes on Procedures

1. It may be necessary to take a smaller or larger amount of solution than the 2 ml indicated in the procedure depending on the individual sample. Water should be added, if necessary, to total 5 ml.

2. The conditions specified should be strictly adhered to in order to obtain consistent results.

3. Avoid too vigorous shaking as emulsification may occur.

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